

THE IDEAS OF PHYSICAL CHEMISTRY

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THE IDEAS OF PHYSICAL CHEMISTRY

BY

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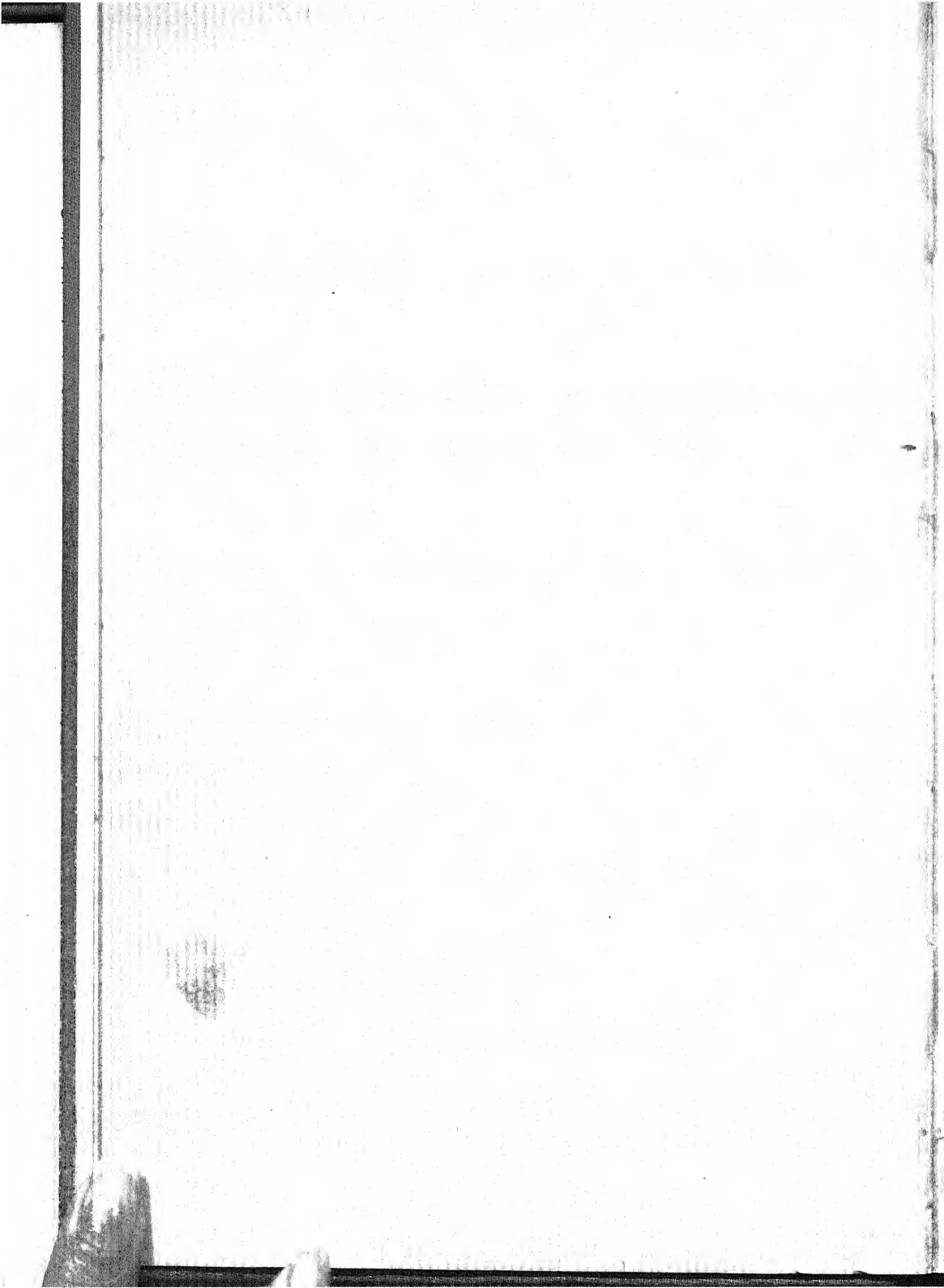
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TO THE AUTHORS'
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THE IDEAS OF PHYSICAL CHEMISTRY

[Passages in square brackets are not essential to an understanding of the subject. They will, however, be found useful by students.]

CHAPTER I

THE ULTIMATE PARTICLES

THE search for the ultimate particles of matter is no new thing. Aristotle conceived of all matter as being composed of four elements : earth, air, fire, and water. The Greeks gave us, too, the idea of the atom as the final and indivisible particle of matter. The early, crude theory of four elements persisted, with modifications, throughout and beyond the Middle Ages. It was not, indeed, until the year 1808 that Dalton revived the idea of the atom and placed the atomic theory on a quantitative basis. Atoms were the ultimate particles of which all matter is composed ; the number of different kinds of atoms was comparatively small (we now know about ninety different kinds). Every compound was made up in the last analysis of atoms of two or more different kinds ; while the elements consisted of one kind of atom only. Each element was distinct from every other element.

These theories held the field for nearly a century. Indeed, many of Dalton's postulates are still unchallenged. Modern work has perfected rather than supplanted them.

It soon began to appear that the elements, though distinct, are not unrelated entities. It was found possible to associate certain of the elements into groups by virtue of resemblances between them ; certain properties run through these groups with regular gradations from element to element. In 1869, Mendeléev produced his periodic table, which extended this grouping of the elements so as to include all the known elements. This table arranged the elements in an ordered sequence and showed how their properties depend on their

positions in this sequence. Mendeléeïev even indicated whereabouts gaps should be left for unknown elements, and predicted the properties of the elements to fill these gaps; many of these predictions have since been confirmed. Mendeléeïev's original table has been modified in detail, but it remains in all its essentials just as he discovered it. A truly great achievement!

There must be some underlying similarity in the structure of all the different kinds of atoms, to explain why the elements can be arranged in the periodic table. But as soon as we admit that the atom has a structure we must give up the idea that the atoms are the ultimate particles of matter. There must be something beyond the atom, something still more fundamental, out of which all the different kinds of atoms are built.

Towards the end of the nineteenth century, J. J. Thomson discovered the electron. When an electric discharge is passed through a highly evacuated tube, "rays" are emitted in straight lines from the cathode (the negative electrode). When these "cathode rays" are submitted to electric and magnetic fields they are deflected from their straight path; Thomson explained this by supposing that the "rays" are really particles, each with a small negative electric charge. He called these particles "electrons." From the amount of their deflection in an electric and in a magnetic field, he was able to calculate the ratio of the charge to the mass of an electron. This ratio is the same for all electrons [except very high-speed electrons], a strong indication that the electrons are all alike.

To find the actual charge and mass of an electron, and not merely their ratio, it is necessary to observe the electrons singly; Thomson had observed them only *en masse* in the cathode rays. Millikan was the first to make these measurements really accurately; he sprayed the electrons with a fine spray of oil drops; one or more electrons adhered to the tiny drops, so that particles were obtained with a charge once, twice, or more times, the electronic charge; these particles were large enough to be visible under the microscope. Millikan measured the rate of fall of these charged

oil drops, first under gravity alone and then in electric fields of various strengths. From these measurements he was able to calculate the charges on the oil drops. He knew these were various integral multiples of the electronic charge, so it was simply a matter of picking out the right multiple. Having found the charge, it was an easy matter to obtain the mass of an electron, for the ratio of these two quantities was known. The mass turned out to be the $1/1840$ th part of the mass of the hydrogen atom. Here then was a particle lighter than the lightest of the elements.

The electron is a universal constituent of matter. Electrons can be obtained : by electric discharges in gases at very low pressures, by the action of ultra-violet light on metals, in flames, from heated metal filaments, by means of

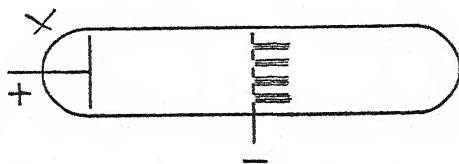


FIG. 1.—Streamers of positive rays passing through perforations in the cathode. From Mee's *Physical Chemistry* (Heinemann).

X-rays, and from radioactive substances. The electrons obtained in all these ways have the same mass and the same charge : so they are all alike (except in velocity).

Electrons must thus be present in all atoms. This can be confirmed by observing atoms from which one or more electrons have been removed. Since the electrons are negatively charged, such atoms are positively charged ; they are called positive ions. Negative ions, atoms to which one or more electrons have been added, are known as well. Positive ions of high speed are produced in a discharge tube along with electrons ; they are then called positive rays. They can be observed by using a perforated cathode in the discharge tube ; they travel in the opposite direction to the electrons, so they pass through the perforations in the cathode, and can be observed as faint streamers of light behind it. They have been investigated, like the electrons, by observing their deflections in an electric and

in a magnetic field ; from their masses and charges it is deduced that they are atoms which have lost one or more electrons.

Ions, atoms or groups of atoms with one or more charges, either positive or negative, are known in solution too. We can show that the charges on these ions are integral multiples of the charge on an electron ; so they are evidently produced from the neutral atom by the removal or addition of electrons. Here is confirmation from an entirely independent source that atoms contain electrons which are relatively easy to remove.

Now the atom is ordinarily electrically neutral ; it has no charge as a whole. There must, therefore, be a positive charge somewhere in the atom to balance the negative charges of its electrons. Rutherford was able to show that this positive charge is concentrated in a small nucleus at the centre of the atom. He did this by bombarding the atom with high-speed alpha-particles, particles which are positively charged. (He actually bombarded with alpha-particles a thin layer of the element in question.) He found that most of the alpha-particles went very nearly straight through the atom ; indicating that the atom is extraordinarily "empty." A few, however, passed very close to the minute nucleus at the centre : the nucleus and the alpha-particle are both positively charged, so they repelled one another, and the alpha-particle was considerably deflected from its path. But most of the alpha-particles do not pass near enough to the nucleus for this to happen.

The atom, then, consists of a small positive nucleus with electrons revolving round it. This idea is quite reasonable : there is the analogy of the solar system, consisting of the sun with the planets revolving round it in elliptical orbits.

The hydrogen atom is the lightest and simplest of all atoms. It has a single electron with a negative charge, and this electron revolves round a nucleus with a positive charge. This nucleus is called the proton ; the proton is the unit of positive electricity just as the electron is the unit of negative electricity. When we say that an atomic

nucleus has, say, four positive charges, we mean that its charge is four times as great as the charge on a proton.

Nearly all the mass of the hydrogen atom resides in the proton. The electron, as we have seen, contains only the 1/1840th part of the mass of the hydrogen atom, so the rest of the mass must be contained in the nucleus. This is confirmed by a determination of the ratio of the mass to the charge of a proton. This ratio is found to be 1840 times as big as the corresponding ratio for the electron; as both these particles have the same charge, this must be due to the mass of the proton being 1840 times as big.

The nuclei of the other elements have bigger positive charges than has the proton. They must have, because their charges have to balance a larger number of negative charges on the electrons revolving round them. The first estimate of the number of positive charges on the nuclei of the elements was made by Rutherford, from his bombardment experiments. He was able to show, roughly, that the positive charge was in each case an integral multiple of the charge on the proton. Thus the helium nucleus has a charge of two units, the lithium nucleus a charge of three units, and so on.

This was confirmed conclusively by Moseley in 1913. Moseley showed that there is a number, the "atomic number," characteristic of each element. If the elements are arranged in order, the same order as that of the periodic table, and then numbered off—one, two, three, four, etc.—we get the atomic numbers of the elements. Moseley

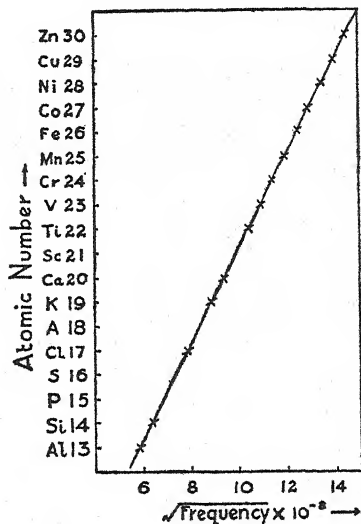


FIG. 2.—The relation between X-ray frequencies and atomic numbers. The straight line shows that there is a simple relation between them.

arrived at the idea of atomic numbers in the following way. He bombarded one element after another with high-speed electrons. Under this bombardment they emitted X-rays ; the frequency of these X-rays proved in each case to be characteristic of the element bombarded. He noted the frequency of the hardest X-rays emitted by each element, that is to say, the rays of greatest frequency. And now came the surprising discovery. He plotted the square roots of these greatest frequencies against the atomic numbers of the elements in question. The graph obtained was a straight line : the frequencies were related in a simple manner to the atomic numbers.

This showed that the atomic number is a fundamental constant characteristic of the atom. The atomic number is about equal to the number of positive charges on the nucleus, as measured by Rutherford. The two can be identified with confidence, any small discrepancies being put down to experimental error in the Rutherford method of determining the charge on the nucleus.

This idea that the atomic number is equal to the number of positive charges on the nucleus received confirmation in other directions, particularly from investigations in the field of radioactivity.

About the same time that the electron was discovered, in the nineties of the last century, it was discovered that certain of the heaviest elements emit " rays " of various kinds. These rays are of three kinds : alpha-rays are the nuclei of helium atoms, with two positive charges—that is to say, they are helium atoms that have lost their two electrons ; beta-rays are electrons ; and gamma-rays are rays of the same nature as X-rays. Alpha- and beta-rays are not really rays at all, but streams of fast-moving particles.

The helium nuclei and electrons given out by the radioactive elements come from the nuclei of these elements. (There are, in addition, secondary beta-rays, electrons which have come from outside the nucleus ; but these do not concern us here.) Now both alpha-particles and electrons are charged particles, so their emission must alter the charge on the nucleus. This means that the identity of the

element is changing. Radium, for example, emits alpha-particles—helium—and changes into radium emanation. The radium atom is in fact splitting up spontaneously, and we must definitely give up the idea of the immutability of the elements.

Alpha-particles have each two positive charges ; so the charge on the nucleus decreases by two units when an atom emits an alpha-particle. In other words, its atomic number decreases by two units ; the element changes into another element two places lower down in the periodic table. An electron has a single negative charge ; so the positive charge on the nucleus increases by one unit when a nucleus emits an electron. The atomic number increases by one unit, and the element moves one place higher up in the periodic table.

The steps in the disintegration of uranium illustrate these changes. The α 's and β 's indicate the particles emitted at each stage :

Atomic number.

92	Uranium I								
91		$\downarrow \alpha$							
90	Uranium X ₁		$\rightarrow \beta$	Uranium X ₂		$\rightarrow \beta$	Uranium II		
89							$\downarrow \alpha$		
88							Ionium		
87							$\downarrow \alpha$		
86							Radium		
							$\downarrow \alpha$		
							Radium emanation		

It will be seen that in every case in which an alpha-particle is emitted, the element goes down two places ; when a beta-particle is emitted, it goes up one place. The strength of this argument lies in the fact that the elements in this series are allocated to just those positions to which we should allocate them by reason of their chemical properties.

We have thus arrived at the idea of the atom as consisting of a small, positively charged nucleus, with a number of negatively charged electrons circulating round it. In the neutral atom the positive charge on the nucleus just balances the sum of the negative charges on the electrons. If we write N for the atomic number of the element, and $-e$ for the

charge on an electron, then in the neutral atom : there is a nucleus with a charge $+Ne$ and outside the nucleus there are N electrons, each with a charge $-e$.

We have still to account for the masses of the different kinds of atoms. We have no longer to account for fractional masses, because the discovery of isotopes (dealt with in the next chapter) has shown that the masses of the atoms are all very nearly whole numbers. Suppose we have an atom of mass A and atomic number N ; both A and N are whole numbers. Its nucleus has, we know, a positive charge of N units and, since most of the mass of an atom resides in the nucleus, it has a mass of A units.

This was originally explained in the following way. The nucleus must contain A protons to give it the necessary mass. (The mass of the proton is unity on the scale used to measure atomic masses ; so that when we say an atom has a mass A , we mean that it weighs A times as much as a proton.) But this would give it a positive charge of A units ; so it must contain also enough electrons to reduce its charge from A to N units, $A - N$ electrons in fact.

This was the argument. It was based on the assumption that the proton and the electron are the only ultimate particles out of which atoms are built. But even then there was the possibility that the alpha-particle, for example, might be a third ultimate particle ; after all it is often emitted intact from the nuclei of the radioactive elements. Of course, there was no definite evidence against the view that the alpha-particle is built up of protons and electrons. Helium has an atomic weight of 4 and an atomic number of 2. ($A = 4, N = 2$.) So the helium nucleus, the alpha-particle, might be composed of 4 protons and 2 ($= 4 - 2$) electrons.

In 1931 the neutron was discovered. When beryllium is bombarded with swift alpha-particles, it emits a weak radiation of great penetrating power. This radiation has been found to consist of high-speed particles of a new kind. They have about the same mass as protons. But they are not deflected by an electric field ; so they can have no electric charge, they are neither positive nor negative. They are

called neutrons in reference to the fact that they are electrically neutral—without a charge.

The discovery of the neutron opens up the possibility that it is one of the ultimate particles out of which atomic nuclei are built. It might of course be a proton embedded in an electron—this would account for both its mass and its lack of charge—but on the whole this is improbable. Neutrons, anyway, have been obtained from atomic nuclei, and quite likely form an essential part of the structure of the nuclei; they would account for some of the mass without adding to the charge. An alpha-particle, for example, has been considered as consisting of four protons and two electrons; the four protons give it the required mass of four, and the two electrons reduce the net charge to two, as required by the atomic number. But an alternative, and perhaps better, explanation is that the alpha-particle consists of two protons and two neutrons; the two protons give it the necessary charge, and the two neutrons make up the mass to four units.

A further addition must also be made to the list of ultimate particles—the positive electron, or positron. For some time it has been known that there is a radiation of extraordinary penetrating power, which appears to come to the earth from outer space. This radiation is often spoken of as the cosmic radiation. It has the power to ionise gases, to break off electrons from the molecules of the gas and so give the molecules electric charges.

So far the properties of the cosmic rays, their penetrating power and their power of ionising gases, do not give us much clue to their nature; these properties are shared by X-rays and other rays of very short wavelength, and by high-speed particles such as the alpha- and beta-rays emitted by radioactive elements. The cosmic rays might, therefore, be either true radiation (like X-rays) or else a stream of high-speed particles.

At first the former view was the more widely accepted. But recently it has been found possible to investigate the effect of a strong electric field on the rays. They are deflected, and in such a direction as to indicate that they

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consist of a stream of positively charged particles. Their mass and charge turn out to be about the same size as the mass and charge of an electron, except that the charge is of the opposite sign.

There thus appear to be four ultimate particles : proton, electron, neutron, and positive electron. Their properties are set out in the following table :

	Charge.	Mass.
Proton.	$+e$	M
Electron	$-e$	m
Neutron	0	M (approx.)
Positive electron (positron) .	$+e$	m (approx.)

These four particles cannot be entirely unrelated. Why do there exist two particles of about the same mass, but of opposite charge, the electron and the positron ? And why do there exist two particles of about the same mass, the proton and the neutron, such that one is charged but the other is electrically neutral ?

One of the most interesting theories which set out to explain the relationship between these particles is due to Dirac. It was put forward before the neutron and the positron were discovered.

In working out a mathematical theory of electrons he found—as was to be expected—solutions of his equations, corresponding to positive kinetic energy (that is, energy of motion). But he found also an infinite number of solutions corresponding to negative kinetic energy. This was surprising. The idea of particles having negative kinetic energy is contrary to our conceptions of energy, and we must look for some explanation of this unusual phenomenon. Moreover, it would be expected that all electrons would fall into these states of negative energy and emit radiation in doing so. But electrons do not do this.

Dirac explained these difficulties in a very bold manner. He supposed that nearly all the negative kinetic energy states are filled up, so that the electrons cannot drop into

them. Yet we cannot perceive the effect of all the electrons in these negative kinetic energy states, because they are distributed evenly in space. Occasionally, however, there is a "hole," a negative kinetic energy state which is not filled up. Dirac suggested that these "holes" are protons. This theory raised many difficulties, but Dirac was able to explain them all away; all but one—why has not the proton the same mass as the electron?

The discovery of the positron cleared up this last remaining difficulty, and indeed confirmed Dirac's theory in a startling manner. Here was a particle of the same mass but of opposite charge to an electron; just the thing for a "hole."

Dirac's theory suggested that an electron and a positron might annihilate one another and disappear in a puff of radiation. Or, conversely, radiation might generate an electron and a positron: this suggests that the number of electrons should be equal to the number of positrons. For this to be true of the atom we are driven to the conclusion that the proton consists of a positron and a neutron; the neutron gives it the necessary mass, and the positron gives it the necessary charge. Then since the number of protons in the atom is equal to the number of electrons, the number of positrons is equal to the number of electrons.

CHAPTER II

ISOTOPES

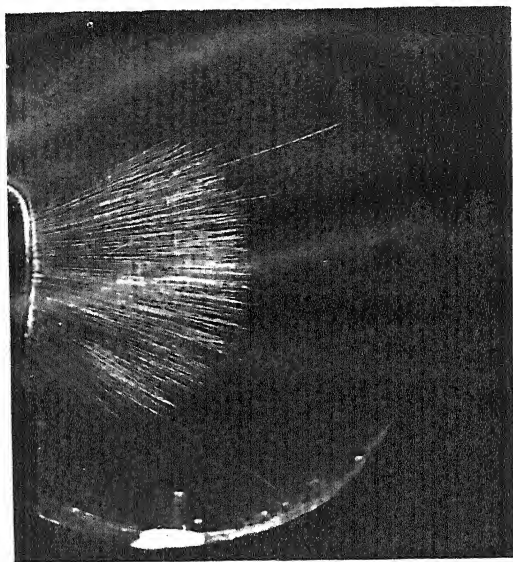
THE discovery of isotopes was one of the most exciting events in the history of physical chemistry. It had always been supposed that all the atoms of an element were identical. It was known that they were very nearly identical in nearly all their properties, for it would be expected that any appreciable difference in properties would allow of a separation of the atoms of an element into two or more different sorts.

That the atoms of an element may be of several kinds, differing in certain properties, became clear from a study of the radioactive elements. The radioactive elements possess the very interesting property of being able to change spontaneously into other elements. Radium, for instance, decomposes spontaneously yielding helium and radium emanation. Now these changes are accompanied by the emission of particles with very high speeds. These particles are either the nuclei of helium atoms (alpha-rays) or electrons (beta-rays).

The speed with which these particles are emitted is characteristic of the element in question. Actually we cannot measure the speed directly, but we can measure how far the particles manage to travel before they are brought to rest. This distance is known as the range of the particles. Thus the range in air of the alpha-particles (helium nuclei) emitted by the radioactive element ionium is 3.194 cms., while that of the alpha-particles from thorium is 2.72 cms.

There is thus an obvious difference in properties between ionium and thorium ; it is, moreover, one which can be used to measure how much of each of these elements is present in a mixture of the two. Now here is the surprising thing. If ionium is mixed with thorium, it is impossible to separate them again by any chemical process. Yet it would be easy

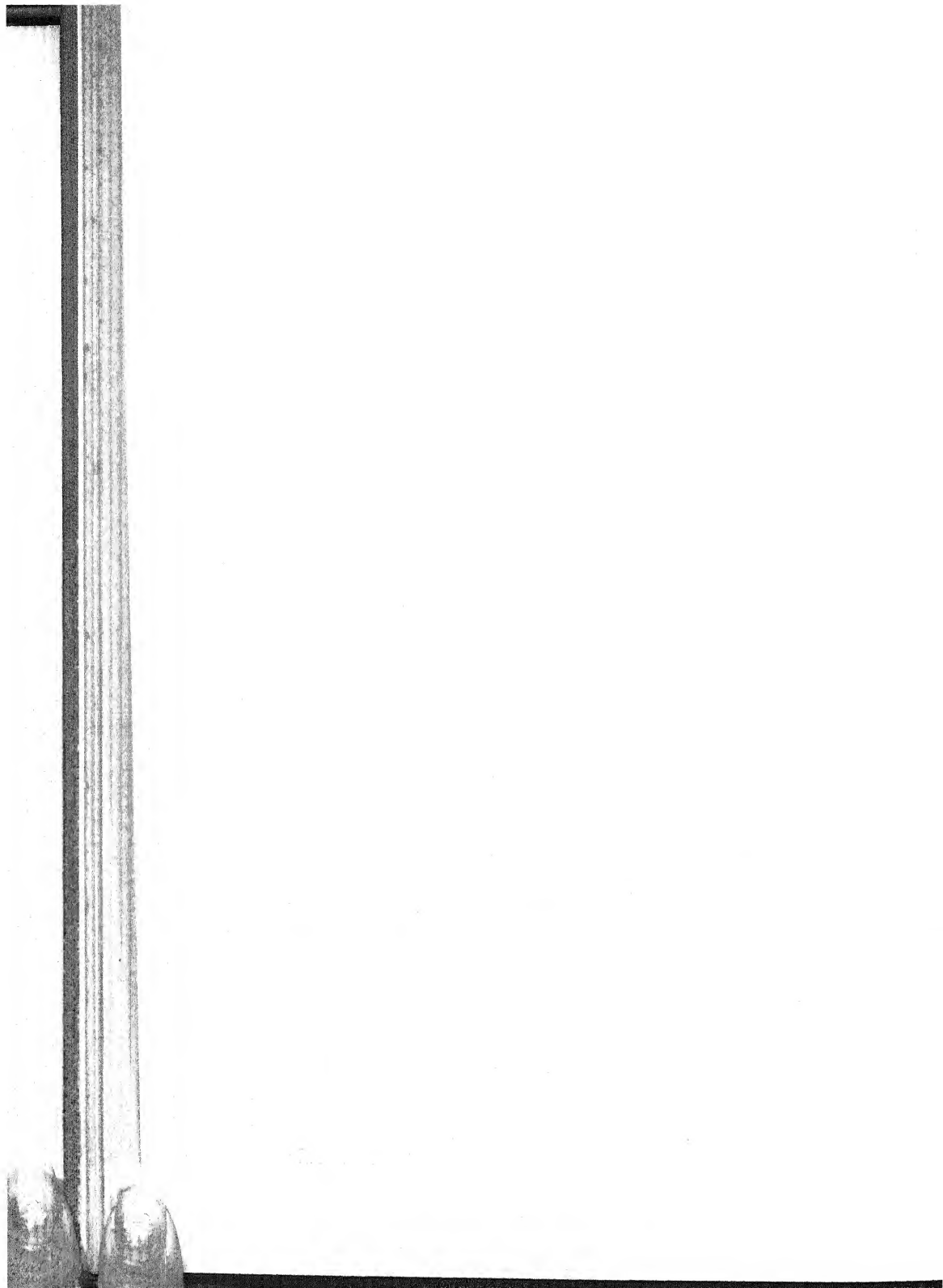
PLATE I.



RANGE OF α -RAYS.

Each alpha-particle that is emitted by the radioactive substance makes a track on the photographic plate; the tracks are all straight. The photograph shows a large number of tracks, and it can be seen that they are all very nearly the same length. The length of the track is the range of the alpha-rays.

(From Hevesy and Paneth's "A Manual of Radioactivity," translated by R. W. Lawson. *By kind permission of the Clarendon Press.*)



to detect even a very small separation, by examining the emitted alpha-particles.

We have thus a pair of elements alike in all their properties except as regards their radioactive behaviour and their atomic weights: ionium has an atomic weight of 232, and thorium, of 230.

This suggests that we might meet similar cases among elements that are not radioactive. But here we shall have only the difference in atomic weight to go by; we shall no longer have the valuable radioactive methods of distinguishing between the different kinds of atoms.

Lead was the first non-radioactive element which was shown to consist of more than one kind of atom. Lead is the final product formed as a result of the disintegration of the radioactive elements. Lead formed by the disintegration of radium has an atomic weight of 206, while that formed from thorium has an atomic weight of 208; ordinary lead has the intermediate value, 207.2. Thus we have the remarkable fact that the atomic weight of lead depends on where it comes from. If we extract the lead from a radium mineral, we find that its atomic weight is abnormally low, less than 207.2; while lead from thorium minerals has an abnormally high atomic weight.

These two forms of lead, of masses 206 and 208, are called the isotopes of lead. Ordinary lead is a mixture of these and other isotopes. Ionium and thorium are similarly said to be isotopes of one another. The isotopes of a non-radioactive element are very nearly alike except in their atomic weights and in properties depending directly on the atomic weight.

Owing to this great similarity in properties, the isotopes of an ordinary element are always mixed together in the same proportion in nature. The only known cases in which even a partial separation of the isotopes exists naturally, are among the radioactive elements and in the exceptional case of lead of radioactive origin. Special methods have therefore to be employed to establish the existence of isotopes.

The most important instrument for this purpose is the

mass-spectrograph, which was devised by Aston. The atoms of the element under investigation are caused to assume an electric charge (to ionise) and are set moving with a very high speed. Now the high-speed atoms of the isotopes of the element differ in mass and they also differ in velocity; we are interested in the differences in mass only, and we want to sort out the atoms according to their masses. We do this by deflecting them first in an electric and then in a magnetic field. If the fields are of the right strengths, all particles of the same mass will be focussed on the same spot, whatever their velocities. Now all these

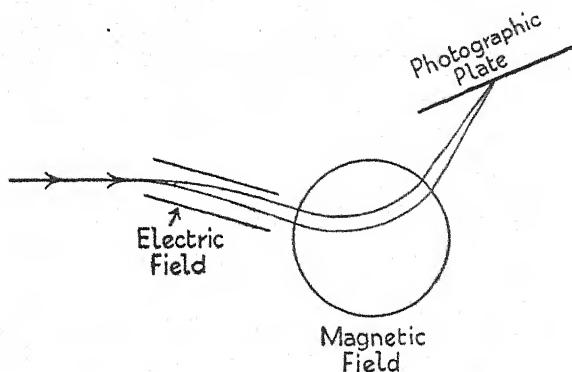
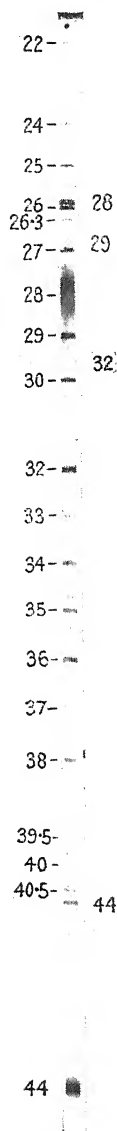


FIG. 3.—Diagram showing the arrangement of the parts in the mass-spectrograph.

particles are travelling at high velocities and they are able to affect a photographic plate. If the particles are focussed on to the photographic plate we shall get a line on the plate whose position corresponds to the mass of the particles. If we have several sets of particles of different masses, each set will give its own particular line on the plate. The series of lines obtained in this way is known as a mass-spectrum.

When chlorine, for example, is examined in the mass-spectrograph, we get two lines. From the positions of these lines we can calculate that these correspond to particles of masses 35 and 37, so we conclude that chlorine is a mixture of isotopes of these masses. It is convenient to write Cl^{35} and Cl^{37} to refer to these two isotopes.

PLATE II.



A TYPICAL MASS SPECTRUM.

The lines marked 35 and 37 are due to the two isotopes of chlorine, Cl^{35} and Cl^{37} . The lines 36 and 38 are due to the hydrides of these isotopes, HCl^{35} and HCl^{37} .

(From Aston's "Mass Spectra and Isotopes" (Plate VI., No. 6). By kind permission of Messrs. Edward Arnold.)

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Another method, particularly valuable for detecting isotopes present in very small quantities, is based on the study of molecular spectra. Consider the two molecules HCl^{35} and HCl^{37} .

HCl^{37} contains a heavier chlorine atom than HCl^{35} , so that the molecule vibrates more slowly. This shows itself in the spectrum of HCl , which is, of course, a mixture of HCl^{35} and HCl^{37} . Each line in the spectrum is split into two lines in slightly different places corresponding to the different rates of vibration of the two kinds of HCl molecule. The distance between the lines, the "separation," is precisely that calculated for the two molecules HCl^{35} and HCl^{37} .

It was in this way that it was shown that oxygen is a complex element and contains the isotopes O^{17} and O^{18} in addition to O^{16} . The former two isotopes are present in very small quantities—oxygen contains only 0.05 per cent. O^{17} and 0.2 per cent. O^{18} —so they are difficult to observe in the mass-spectrograph. There is the additional difficulty that O^{17} and HO^{16} , and O^{18} and H_2O^{16} are of the same mass and can hardly be distinguished in the mass-spectrograph. In the spectrum of oxygen gas (O_2) the lines due to the preponderating $\text{O}^{16}\text{O}^{16}$ molecules are accompanied by faint lines due to $\text{O}^{16}\text{O}^{18}$ molecules, and still fainter lines due to $\text{O}^{16}\text{O}^{17}$ molecules.

The discovery of isotopes effected a remarkable simplification in problems of atomic structure. Throughout the nineteenth century scientists had puzzled over the problem of atomic weights. Why are so many of them very nearly whole numbers, whilst others are obviously a long way from whole numbers? Chlorine was one of the most glaring exceptions to the whole number rule, having an atomic weight of 35.46.

The knowledge that chlorine consists of the isotopes Cl^{35} and Cl^{37} explains the apparent anomaly. Both the isotopes have atomic weights which are very nearly whole numbers, but ordinary chlorine contains them mixed in the proportion of roughly 3 parts of Cl^{35} to 1 part of Cl^{37} . This gives the observed atomic weight for the mixture. The

constancy of the observed atomic weight is accounted for by the fact that the isotopes have identical chemical properties and have had plenty of chance of getting thoroughly mixed together (*e.g.*, as common salt, NaCl , in the sea).

The particular atomic problem of isotopes, then, is : how can atoms be identical in chemical properties but yet differ in mass ? The statement that the isotopes of chlorine, for example, are identical is equivalent to saying that Cl^{35} and Cl^{37} have the same atomic number—actually 17. The atomic number is equal to the net number of positive charges on the nucleus ; in the neutral atom it is equal also to the number of electrons outside the nucleus. Both Cl^{35} and Cl^{37} have the same positive charge on the nucleus, 17, and the same number of electrons outside the nucleus, again 17. It is, of course, these 17 electrons which give the chlorine atom its particular chemical properties.

This settles why Cl^{35} and Cl^{37} are alike in chemical properties. Their difference in mass must be due to a difference in their nuclei, where most of the mass resides. The two kinds of Cl nuclei have, then, each a net positive charge of 17, but one has a mass 2 units greater than that of the other. It is probable that the extra mass arises because it contains two neutrons more. (Neutrons are neutral particles having a mass of 1 unit.) Of course, we could also make up the extra mass by means of 2 protons and 2 electrons : this would leave the net charge unaffected, for the charge on a proton is exactly equal and opposite to that on an electron.

If we assume that the chlorine nuclei are built up out of protons and neutrons only, the constitutions of the Cl^{35} and Cl^{37} atoms become :

	Cl^{35}	Cl^{37}
Outside the nucleus .	17 electrons	17 electrons
In the nucleus . . .	{ 17 protons 18 neutrons	{ 17 protons 20 neutrons

This gives the masses 35 ($= 17 + 18$) and 37 ($= 17 + 20$) as required.

To the chemist, the problem of the separation of isotopes is a matter of considerable interest. As already mentioned, the isotopes of an element are never even partially separated in nature, unless the element is of radioactive origin. Many samples of iron, for instance, have been examined, including iron from meteorites. In every case the iron had the same atomic weight. Meteoric iron proved to be identical with terrestrial iron, having just the same proportions of isotopes. This shows that, at any rate throughout the colder parts of the solar system, not even a slight separation of isotopes is to be expected. It is likely that if nature cannot separate isotopes, the chemist is at least going to find it a very difficult problem. The mass-spectrograph does indeed achieve a complete separation, but the amounts so separated are extremely minute. Recently the two isotopes of lithium, Li^6 and Li^7 , have been separated by this method. Sufficient was separated for the bombardment experiments described in the next chapter—not, however, sufficient for ordinary chemical experiments.

One of the earliest successes was the partial separation of the isotopes of neon by Aston. Neon is one of the inert gases of the air. It consists of two isotopes Ne^{20} and Ne^{22} ; there is thus a 10 per cent. difference in atomic weight, and hence in density. As a result of this difference in density, Ne^{20} diffuses more rapidly than Ne^{22} . Aston allowed the gases to diffuse at low pressure through a clay tube, and obtained samples of neon of densities 20.15 and 20.28. This showed clearly that a partial separation had been achieved.

The most successful way of separating isotopes is by the method known as ideal distillation. In this process the liquid is allowed to evaporate very slowly and is condensed on a cold surface only one or two centimetres away. The liquid is heated very gently electrically, and the condensing surface is kept cold by liquid air.

When a liquid is allowed to evaporate, the lighter atoms move faster than the heavier atoms, so that they come off from the liquid more readily. But in ordinary distillation, the vapour and the liquid are very nearly in equilibrium,

so particles are travelling both from the liquid to the vapour and in the opposite direction. The lighter atoms evaporate from the liquid surface faster than the heavier, but they also return from the vapour to the liquid faster. The two effects very nearly cancel one another out. In ideal distillation, the return of atoms from the vapour to the liquid is cut down as far as possible. The evaporation is carried out at a very low pressure so that the atoms do not often collide and get reflected back to the liquid, and the condensing surface is very close to the evaporating surface for the same reason. When once molecules have reached the very cold condensing surface, they have, of course, no chance of going back to the liquid again. To obtain a

measurable separation it is essential to repeat the ideal distillation a number of times.

Mercury was the first element whose isotopes were partially separated by means of ideal distillation. Potassium was also investigated in this way. Potassium is feebly radioactive, and it was

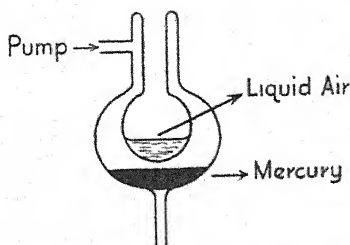


FIG. 4.—The method of ideal distillation. The tube below is used for introducing the mercury.

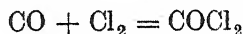
desired to find out which isotope, K^{39} or K^{41} , was responsible for the radioactivity. After ideal distillation, an increase in the radioactivity of the heavier fraction was observed, and the increase was just what would be expected if the radioactivity were a property of K^{41} .

A very interesting suggestion for the separation of isotopes was made by Prof. Merton. When light is passed through chlorine, the gas absorbs light of certain particular wavelengths; this is why chlorine is greenish-yellow. Since there are two kinds of chlorine molecules, Cl_2^{35} and Cl_2^{37} , light of two slightly different wavelengths is absorbed. The Cl^{35} isotope preponderates, so light passed through chlorine allows more of the wavelengths corresponding to Cl^{37} to pass through it. (There are also $Cl^{35}Cl^{37}$ molecules, but this does not affect the general argument.)

When light falls on a mixture of chlorine and hydrogen the two gases react and form hydrogen chloride. If, instead of ordinary light, we use light partially filtered through chlorine, more of the Cl^{37} than of the Cl^{35} isotope might react. The result would be the production of hydrogen chloride containing more of the heavier isotope than usual.

This suggestion was tried out without success. What happens when the chlorine is illuminated is that each Cl_2 molecule that absorbs light splits up into two Cl atoms. The reaction starts from these atoms and continues throughout the whole mass of the gas. [It is a chain reaction.] Probably more Cl^{37} atoms than Cl^{35} atoms were formed initially, but they would be lost in comparison with all the molecules which reacted subsequently to give HCl .

Recently the experiment has been successfully repeated using a different reaction, the combination of carbon monoxide and chlorine to give phosgene. In this case only those molecules of chlorine which initially absorb light actually react, so the complications of the hydrogen and chlorine reaction do not arise. [The reaction is :—



It is not a chain reaction.]

HEAVY HYDROGEN.—There are still discoveries to be made about the most familiar substances. The discovery of the inert gases in the air is a case in point ; these gases constitute about 1 per cent. of the air, and yet they had been overlooked until the nineties of the last century. Just as surprising is the recent discovery that hydrogen—and along with it all its compounds, including water—is complex. It consists, in fact, of two isotopes, one twice as heavy as the other.

This may not seem very remarkable ; most elements consist of mixtures of isotopes, but this has no appreciable effect on their ordinary chemical properties. With hydrogen, however, the case is rather different, for the difference in properties between the two isotopes is remarkable. In most cases there is not more than 10 per cent. difference in mass between the isotopes, and the corresponding difference in

properties is almost negligibly small ; but in the case of hydrogen there is a 100 per cent. difference in mass, and a relatively large difference in properties.

Of course, the heavy isotope of hydrogen is not present in ordinary hydrogen except in small quantities, say 1 part in 6,000. This is one of the main reasons why it was for a long time overlooked. It was originally discovered spectroscopically, this being the best way of detecting isotopes present only in small proportion : the lines in the spectrum due to the heavy isotope are in slightly different places from those due to the light isotope.

The great interest of "heavy hydrogen" lies in the fact that it can be completely separated from ordinary hydrogen ; with no other element is there sufficient difference in properties to enable more than a slight separation of isotopes to be achieved.

The most useful way of concentrating the heavy isotope is by the electrolysis of water. The discovery of this method was to some extent a matter of luck. The discoverers were able to obtain a sample of water from an old electrolytic cell which had been running for several years. They found that the density of this water was distinctly higher than usual, indicating that it contained more of the heavy isotope of hydrogen than does ordinary water. This was encouraging ; here was the simplest method yet proposed for separating the isotopes of any element.

During the electrolysis, hydrogen comes off at one electrode and oxygen at the other. The light isotope of hydrogen comes off at a rate some five times as fast as does the heavy isotope ; so the proportion of the heavy isotope in the water left behind increases steadily. All that is necessary is to go on electrolysing the water for a sufficient time, and as pure a sample of "heavy water" as is desired can be obtained. The progress of the separation can be followed by finding the density of the water. Water containing 30 per cent. of the heavy isotope is now on the market for the use of physical chemists.

If very pure heavy hydrogen is desired, a diffusion method is available. It is claimed that heavy hydrogen

produced in this way is so pure that none of the ordinary isotope can be detected in it spectroscopically; yet this is one of the most sensitive methods of detecting traces of impurities, etc.

There are several remarkable differences in properties between heavy hydrogen and ordinary hydrogen, and between heavy water and ordinary water. Heavy water, consisting of H_2^{18}O molecules instead of H_2^{16}O molecules, melts at 3.8°C . instead of 0°C ., and boils at 101.42°C . instead of 100°C .; its viscosity is considerably higher than that of ordinary water; and, perhaps most interesting of all, it has certain toxic properties. Tadpoles die, and tobacco seeds fail to germinate, in heavy water. Nevertheless, these toxic properties do not justify the suggestion, which appeared in the popular press, that heavy water might be used as a lethal spray in warfare. The poisonous effects are noticed only with pure heavy water, and disappear as soon as it is diluted with ordinary water—as it would be if, for example, it were taken internally.

CHAPTER III

TRANSMUTING THE ELEMENTS

CHEMISTRY is concerned almost entirely with the outer electrons of atoms ; it is these outer electrons that give an atom its chemical properties, that decide what compounds it can form and what reactions it can undergo. But the identity of an element depends on the nucleus, the minute complex consisting of protons, electrons, and neutrons that is at the centre of the atom. The net positive charge on the nucleus, the atomic number, identifies the element : a unit charge on the nucleus identifies the element as hydrogen ; a charge of two units identifies it as helium ; a charge of three units, as lithium ; and so on.

There are great difficulties in the way of studying the nuclei of atoms. It is not easy to get at them because they are surrounded by protective sheaths of electrons. The most hopeful way of getting through this armour is to bombard them with high-speed particles. Not many particles could be expected to make a direct hit ; but then it is possible to use billions of particles, so that a few will actually strike the nuclei.

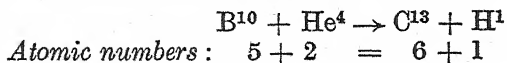
The first high-speed particles to be tried were alpha-particles from a mixture of radium B and radium C ; these particles have a speed about one-twentieth of that of light. In the course of the bombardment there were sufficient direct hits to produce observable results. When an alpha-particle penetrates to a nucleus, the nucleus receives a sudden access of energy, and that may have various results. For one thing, the alpha-particle may simply emerge again unchanged. Or the alpha-particle may be captured by the nucleus, and a proton—a hydrogen nucleus—emitted in its place. Or a proton may be emitted without the capture of the alpha-particle. Any excess of energy in these processes

will be radiated away in the form of radiation of short wavelength.

The liberated hydrogen nuclei are very light and they move with considerable speed. They may be observed by allowing them to impinge on a screen of zinc sulphide; a little flash is seen whenever a high-speed proton strikes this screen.

Whenever an alpha-particle is captured by a nucleus, or a proton is emitted by a nucleus, a change takes place in that nucleus. Both its mass and its charge may be altered; for instance, the ejection of a proton by a nucleus means that it has lost one positive charge and one unit of mass. Now it is the charge on the nucleus that identifies an element; if we change that, we are changing the identity of the element. Here, then, we have a process which enables us to transmute one element into another, although only on a very small scale—too small for the transmutation to be detected by ordinary chemical means.

Boron is one of the elements which have been transmuted by bombardment with alpha-particles; protons are liberated during the process. Boron has two isotopes of masses 10 and 11 (B^{10} and B^{11}); it is the B^{10} isotope which is attacked. When a B^{10} nucleus receives a direct hit, it may capture the alpha-particle (the helium nucleus) and lose a proton (a hydrogen nucleus). The helium nucleus has two positive charges and the proton has one, so the boron nucleus gains on balance one positive charge. This increases the atomic number by 1, from 5 to 6, so that the boron nucleus is converted into a carbon nucleus. The mass of this carbon nucleus is 13. This is made up of the mass of the boron nucleus (10 units) *plus* the mass of the helium nucleus (4 units) *minus* the mass of the hydrogen nucleus (1 unit). The whole process can be written:



The atomic weights on the two sides of the equation balance ($10 + 4 = 13 + 1$), and so do the atomic numbers. Of course, this is not an ordinary chemical equation.

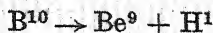
The proton produced in this process can be detected by means of a screen of zinc sulphide, as already mentioned. The carbon nucleus formed at the same time is much heavier, so it moves much more slowly and cannot be detected in this way. The equation for the process enables us to infer that it is formed.

The behaviour of boron is typical of the behaviour of many elements on bombardment with high-speed particles. Nitrogen, for example, behaves similarly, the nitrogen nucleus capturing the alpha-particle and emitting a proton. The nitrogen nucleus gains a positive charge and becomes an atom of oxygen :



$$\text{Atomic numbers : } 7 + 2 = 8 + 1$$

Sometimes, however, other things happen. An alpha-particle may whizz past a nucleus, without actually being captured, and disturb the nucleus so much that it emits a proton. The process is thus simply the disintegration of an atomic nucleus with the emission of a proton ; the alpha-particle actuates the change, but does not take part in it. This process, as well as the process involving the capture of the alpha-particle, is a possible one for the B^{10} isotope. In the present case, the boron nucleus loses one unit of mass and one charge and becomes a beryllium nucleus of mass 9. The equation for the process is :

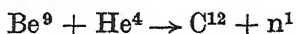


$$\text{Atomic numbers : } 5 = 4 + 1$$

When beryllium is bombarded with alpha-particles a still further process occurs. A direct hit results in the ejection, not of a proton, but of a particle without any charge at all, neither positive nor negative. As it is electrically neutral, this particle is called the neutron and is usually represented by the symbol n . The atomic number of the neutron is 0—this is merely another way of saying that it has no charge—and its atomic weight is unity, like that of hydrogen.

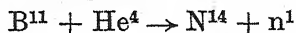
A direct hit, therefore, by an alpha-particle may result in a beryllium atom gaining a helium nucleus and losing a neutron. On balance the beryllium gains two positive

charges so that it becomes an atom of carbon ; and it gains three units of mass, so the carbon atom produced has a mass of 12 units. The process is :



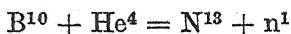
$$\text{Atomic numbers : } 4 + 2 = 6 + 0$$

Neutrons can be obtained by bombarding other elements besides beryllium with alpha-particles. Boron is a case in point. The neutrons come from the B^{11} isotope, whereas the B^{10} isotope ejects protons. Thus the B^{11} atom gains two charges and three units of mass, and becomes an atom of the N^{14} isotope of nitrogen :



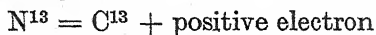
$$\text{Atomic numbers : } 5 + 2 = 7 + 0$$

There is yet another thing which may happen in these bombardments : positive electrons may be emitted. This happens with boron, for example. A very interesting feature is the fact that the boron goes on emitting positive electrons even after the source of alpha-particles has been removed ; the emission continues for an hour or two, getting steadily feebler all the time. The explanation of this is that the new nuclei produced during the bombardment are unstable. In the case of boron, an N^{13} nucleus and a neutron are produced :



$$\text{Atomic numbers : } 5 + 2 = 7 + 0$$

(The atomic weights and the atomic numbers balance as usual.) This N^{13} nucleus is not stable, but breaks up with the emission of positive electrons. It loses one positive charge and only a negligible amount of mass in this process, so it becomes a C^{13} isotope :



$$\text{Atomic numbers : } 7 = 6 + 1$$

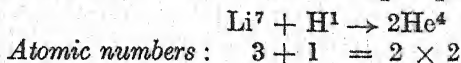
This C^{13} isotope is stable and does not break up any further.

That it really is an isotope of nitrogen that is responsible for the emission of these positive electrons, has been shown in this way. Boron nitride, BN, was bombarded with alpha-particles. Then it was heated with caustic soda ; the

nitrogen came off as ammonia gas (NH_3), and the boron remained behind. It was found that all the positive electrons now came from the ammonia, and none from the residue containing the boron; this proves the point.

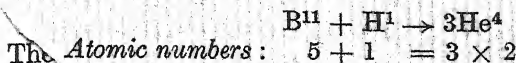
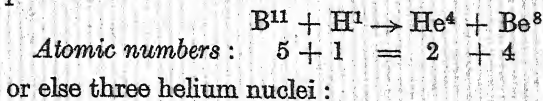
It was natural to look round for other particles besides alpha-particles for these bombardment experiments. The next particles to be tried were protons. Protons are atoms of hydrogen from which the outer electron has been removed; they can be produced by passing an electric discharge through hydrogen in a highly rarefied condition. To be effective in bombardment the protons produced in this way must be given a high velocity; they are accelerated by letting them pass through an electric field with a very high potential drop. The pull of the field on the extremely light protons gives them the necessary high speed.

When lithium is bombarded with swift protons it emits alpha-particles; it is actually the Li^7 isotope which is involved. If a lithium nucleus captured a proton and emitted one alpha-particle, its net loss in mass would be three units, and its loss in charge one unit. As a result, the other nucleus produced is also an alpha-particle:



It was mentioned in the previous chapter that a complete separation of the isotopes of lithium has been achieved; so it has been possible to settle definitely that it is the Li^7 isotope which undergoes this process.

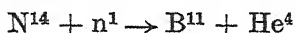
Boron atoms also can capture the fast protons. In this case either one helium nucleus and a Be^8 nucleus might be produced:



The second process might be a result of the first, the Be^8 existing and decomposing as fast as they are formed. The actual existence of the Be^8 isotope of beryllium is a matter still in

doubt. Helium is often found in beryllium minerals ; it has been suggested that this has come from the disintegration of Be^8 and that there is now none of this isotope left in nature.

Besides the alpha-particle and the proton, neutrons have been used to bring about these transmutations. When neutrons are ejected from beryllium, they have a very high velocity and can be used directly in bombardment experiments. For instance, when nitrogen is bombarded with neutrons, it emits an alpha-particle and forms boron :



$$\text{Atomic numbers : } 7 + 0 = 5 + 2$$

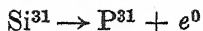
This process is the reverse of one of the processes which take place when boron is bombarded with alpha-particles. Neutrons may also give rise to high-speed protons when they are used to bombard other elements. Neutrons have the advantage over other bombarding particles that they have no charge. The alpha-particle and the proton have positive charges, so they are repelled by the nuclei of the bombarded element.

The new nuclei formed during bombardment with neutrons are often unstable ; they break down and emit electrons. Thus, when phosphorus is bombarded with neutrons, and the source of neutrons is removed, it is found that the phosphorus goes on emitting electrons. In this case the unstable nucleus is a silicon nucleus :



$$\text{Atomic numbers : } 15 + 0 = 14 + 1$$

The silicon nucleus then breaks down :

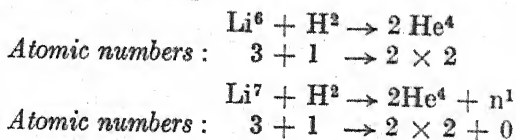


$$\text{Atomic numbers : } 14 = 15 + (-1)$$

(The electron has a charge of *minus* one, so its atomic number is *minus* one.) In some of these processes the unstable nuclei have quite a long "life" : with arsenic the emission of electrons continues for two days after the source of neutrons has been removed.

The discovery of the heavy isotope of hydrogen provides

the possibility of a fourth particle for use in disintegration experiments ; it proves to be more effective than the proton. The nuclei of this isotope have a charge of one unit and a mass of two units. They disintegrate both isotopes of lithium, for example :



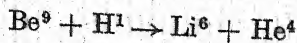
The neutrons emitted in the second process have been definitely detected ; and the separation of the isotopes of lithium has given a further check on these equations.

These transmutations are often accompanied by the emission of energy in the form of radiation. This radiated energy is partly the energy of the bombarding particle and partly comes from the actual conversion of mass into energy. The possibility of such a conversion was foreshadowed by the theory of relativity, which gave the relation that

$$\text{Energy} = \text{Mass} \times (\text{Velocity of Light})^2$$

According to this relation, if the mass of five ounces of matter were converted into energy, we could obtain a million horse-power for one year. For comparison, the Niagara Falls supply energy at the rate of about five million horse-power, so that the conversion of 25 ounces of matter into energy every year would give as much energy as if the whole of the Falls were harnessed. It is evident that the conversion of mass into energy sets free prodigious quantities of energy.

We have said that the atomic weights balance in the equations representing transmutations. This is true only if the atomic weights of the isotopes are taken to the nearest whole numbers. The weights of isotopes are, however, not usually quite whole numbers, so there are small fractional differences between the two sides of the disintegration equations. For instance, the masses involved in the process :



are :

9.016, 1.008, 6.012, and 4.002

so the decrease in mass is 0.010. Thus, if 9 grams of beryllium and 1 gram of hydrogen were converted into lithium and helium, 0.010 gram of matter would be converted into energy ; this corresponds to about 10^{19} ergs, or 10^{12} ft.-lbs. Although the difference in mass is small, it corresponds to an enormous amount of energy and it becomes of great significance.

The transmutation of the elements is the only process known by which mass can be converted into energy. It offers the most reasonable explanation of the enormous amount of energy which is radiated by the sun and stars. The almost incredibly high temperatures within the sun and stars keep the alpha-particles, protons, and other particles, moving at very high speeds ; as high as the speeds used in terrestrial disintegration experiments. The high speeds of these particles in the sun and stars enable them to bring about transmutations just like those we carry out in the laboratory. Some of these processes lead, as we have seen, to the emission of radiation, and this is the most likely source of the enormous amounts of energy given out by the sun and stars. These are gradually frittering away their mass in the form of radiation, but the process is much too slow to cause any really considerable diminution in their size.

CHAPTER IV

THE BOHR THEORY

In the first chapter we arrived at the idea of the atom as a small positive nucleus with electrons revolving round it. This arrangement is like the solar system in extreme miniature. But there is an essential difference—the nucleus and the electrons in the atom are electrically charged.

In 1913 Bohr pointed out that these electric charges introduce a serious difficulty. A body which is travelling in a curved path must have an acceleration towards the centre of the curve; if it were not accelerating inwards it would simply travel on in a straight line. The electrons in the atom must, therefore, be accelerating. But according to "classical" electrodynamics a charged body which is accelerating must be radiating away energy; so the electrons in the atom should be emitting energy continually. This loss of energy would go on until the electron reached the nucleus; just as the planets would fall toward the sun if they were to be slowed down, that is, if they were to lose some of their kinetic energy.

But the electrons obviously do not drop into the nucleus; they go on revolving indefinitely. It is evident that the classical theory of electrodynamics does not apply to the electrons in an atom, and some new theory must be devised more in accord with the observed facts.

Bohr suggested that there are certain states of the atom in which it does not emit any energy whatsoever, although its electrons are still rotating round the nucleus. He called these states "stationary states," because the energy of the atom is, for the moment, stationary (constant) when the atom is in one of these states. This was in flat contradiction to the classical theories, but then classical theories were breaking down in many directions when Bohr put forward his theory.

An atom cannot lose energy indefinitely. If it did we should meet the old difficulty once more: the electrons would, jump by jump, lose the whole of their energy. An atom eventually reaches a state in which it can give up no more of its energy. This lowest possible state is called the lowest electronic energy level or the ground state.

The theory has been worked out in considerable detail for the case of the hydrogen atom; this is a particularly simple case, for there is only one revolving electron. Bohr supposed that the electron can revolve in a limited number of orbits only, each orbit corresponding to a particular stationary state of the atom. There is a condition, known as a quantum condition, which tells us which orbits are possible. This condition involves a number n , called the principal quantum number: thus $n = 1$ gives the smallest orbit of the electron, $n = 2$ gives the next smallest, $n = 3$ the next, and so on; n can have any of the values 1, 2, 3, 4 . . . etc.

The quantum condition is actually that the angular momentum of the electron shall be an integral multiple of $\frac{h}{2\pi}$. Here, h is a constant known as Planck's constant. If n is the principal quantum number, this condition can be written:

$$mvr = \frac{n\hbar}{2\pi}$$

where m is the mass of an electron, v is its velocity, and r is the radius of its orbit.

A second equation can be obtained as follows. The electron has a charge of $-e$ and the proton (the nucleus) has a charge of $+e$; so they attract one another with a force $\frac{e^2}{r^2}$. This force must be equal to the mass of the electron multiplied by its acceleration towards the proton, which is at the centre of its orbit. Putting this in symbols:

$$\frac{e^2}{r^2} = m \times \frac{v^2}{r}$$

These two equations enable us to find separately the

radius r and the velocity v . Eliminating v , we find that r is equal to

$$n^2 \left(\frac{h^2}{4\pi^2 m e^2} \right)$$

But n is equal to 1, 2, 3, etc., so r is equal to 1, 4, 9, etc., times the radius of the smallest orbit.

The energy of the atom is different for different stationary states; it depends on which orbit the electron is in. The smaller the orbit, the less the energy. For this reason the stationary states of the atom are often called electronic energy levels. Now an electron can jump from one orbit to another, or, putting it in other words, the atom can go from one stationary state to another. When this happens the

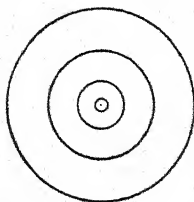


FIG. 5.—Radii of the orbits in the hydrogen atom.

energy of the atom changes; the atom must either emit or absorb energy equal in amount to the difference in energy between the two stationary states. Such energy changes do not take place gradually, but always by a sudden jump. It is like walking up or down a flight of stairs—except that the stairs are not all of the same height—rather than up or down the gradual classical slope.

The quantities of energy which are emitted or absorbed by atoms when they jump from one energy level to another are called “quanta.” Quanta are small “packets” of energy. They are always emitted or absorbed one at a time. Of course an atom may emit or absorb two or more quanta, one after the other; but never a fraction of a quantum.

When an atom emits energy, the energy appears in the form of light; conversely an atom can absorb energy from light. A quantum of light-energy is equal to the frequency of the light multiplied by the constant known as Planck's constant. Denoting the frequency of the light by ν , and Planck's constant by h , we have $h\nu$ for the size of the quantum. The size of the quantum is obviously fixed by the frequency of the light.

Now we have said already that when an atom jumps

from one stationary state to another, one quantum of energy is absorbed or emitted. If E_1 and E_2 are the energies of the atom in the two stationary states, then we can write :

$$E_1 - E_2 = h\nu$$

This is the Einstein equation. It is simply a mathematical way of saying that the quantum which is absorbed or emitted is equal to the difference in energy between two energy levels of the atom.

If we can find the values of E_1 , E_2 , etc., we can use the Einstein equation to calculate the frequency of the light, ν . Bohr was able to calculate the values of all the E 's for the hydrogen atom, and then by combining them in pairs he was able to find all the light-frequencies that the hydrogen atom can emit or absorb.

He found actually that the energy of the atom for a particular electronic orbit

is proportional to $\frac{1}{n^2}$, where

n is the principal quantum number of the orbit in question.

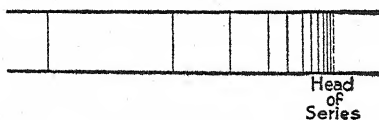


FIG. 6.—Part of the hydrogen spectrum. (After Birtwistle's *Quantum Theory of the Atom*, by permission of the Cambridge University Press.)

To investigate experimentally what frequencies the hydrogen atom can emit, an electric discharge is passed through a tube containing hydrogen at low pressure. The hydrogen glows, and the glow emitted is spread out into a spectrum ; in the spectrum each separate frequency appears as a single vertical line, so it is easy to see which frequencies are present and which are absent. The diagram shows part of the spectrum of hydrogen.

Each line in the spectrum represents an energy change, from some higher energy level in each case to a lower level. In the part of the spectrum shown in the diagram, the lower level is the same for every line. (It is, as a matter of fact, the lowest level but one in the atom.) Now, how is the Bohr theory to account for the positions of these lines ? According to the theory, the energy in any stationary state is equal to

$\frac{k}{n^2}$, where k is a constant, which can be calculated from the

Bohr theory ; so the difference in energy between two stationary states is :

$$\frac{h}{n_1^2} - \frac{h}{n_2^2}$$

(where n_1 and n_2 are the principal quantum numbers for the two orbits). This difference, we have seen, is equal to $h\nu$, so :

$$\nu = \text{constant} \times \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

The constant is usually written as Rc , where R is the so-called Rydberg constant and c is the velocity of light. Thus we get at last the equation :

$$\nu = Rc \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

This equation enables us to find all the values of ν by giving n_1 and n_2 the values 1, 2, 3, etc.

Before Bohr put forward his theory, Balmer had discovered that all the lines in the visible part of the hydrogen spectrum—the part shown in Fig. 6—can be represented by the series :

$$\nu = Rc \left(\frac{1}{2^2} - \frac{1}{3^2} \right); \nu = Rc \left(\frac{1}{2^2} - \frac{1}{4^2} \right); \nu = Rc \left(\frac{1}{2^2} - \frac{1}{5^2} \right); \text{etc.}$$

Bohr's theory accounts very beautifully for this series ; we have only to put $n_1 = 2$, and give n_2 the values 3, 4, 5, etc., in succession, and we obtain it.

Similar series have been found in which n_1 has other values. The series for which $n_1 = 1$:

$$\nu = Rc \left(\frac{1}{1^2} - \frac{1}{2^2} \right); \nu = Rc \left(\frac{1}{1^2} - \frac{1}{3^2} \right); \nu = Rc \left(\frac{1}{1^2} - \frac{1}{4^2} \right); \text{etc.}$$

was looked for after the enunciation of the Bohr theory ; it was found by Lyman in the ultra-violet part of the spectrum, just where Bohr had predicted. The series for which $n_1 = 3$ was discovered by Paschen in the infra-red prior to the Bohr theory ; and a further series for which $n_1 = 4$, lying still farther out in the infra-red, was looked for and found by Brackett.

Bohr's theory, then, leads to a formula of the right kind

to explain the positions of the lines in the hydrogen spectrum, namely :

$$\nu = R c \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

This formula is quantitatively exact, too. According to the Bohr theory, R should be equal to :

$$\frac{2\pi^2 m e^4}{c h^3}$$

Every quantity in this formula can be determined independently of the theory ; it is found that R is equal to 1.09×10^5 . This is in excellent agreement with the value 1.09675×10^5 determined from the positions of the lines in the hydrogen spectrum. (Of course, the spectroscopic method of determining R is much the more precise.)

Bohr's theory can be applied, with slight modifications, to two other kinds of atom also. In both these cases there is but one electron revolving round the central nucleus, just as in the case of the hydrogen atom. The two kinds of atom are the singly ionised helium atom, He^+ , and the doubly ionised lithium atom, Li^{++} . The lines in the spectra of both these atoms are given by the formula :

$$\nu = \text{constant} \times \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

although the constant in this formula differs for different kinds of atom.

The consideration of atoms with more than one revolving electron cannot be carried out so exactly as that of the hydrogen atom, owing to the mathematical difficulties involved. Nevertheless, Bohr's theory has proved of great value, for it indicates qualitatively the kind of behaviour to expect from other atoms.

The lines in the hydrogen spectrum are not sharp and clear-cut. For one thing there is a blurring due to the fact that the atoms are all moving about haphazard. [This is a Doppler effect.] But besides this blurring each line is split up into two or three lines close together ; so close that with ordinary instruments they cannot be distinguished

separately. This splitting into several lines is called the fine structure of the line.

The Bohr theory is capable of explaining the existence of this fine structure. So far we have treated the electronic orbits as though they were all circular; but, remembering the analogy of the solar system, we might quite well suppose that they are sometimes elliptical. So far as ordinary Newtonian mechanics is concerned this makes no difference: the energy of the atom is the same whether the electron is moving in a circular orbit or in an elliptical orbit such that the semi-major axis of the ellipse is equal to the radius of the circle.

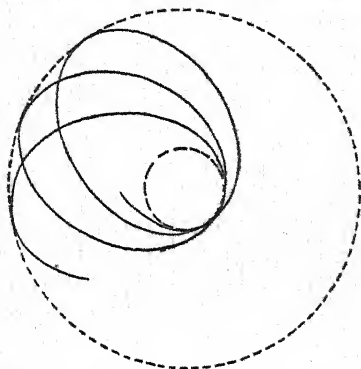


FIG. 7.—The precession of an electron in an elliptical orbit. (After Birtwistle's *Quantum Theory of the Atom*, by permission of the Cambridge University Press.)

The speed of the electron is different at different parts of its orbit, when this orbit is elliptical: it is greatest when the electron is near the nucleus and least when it is far away. This makes no difference in Newtonian mechanics. But according to Einstein's theory of relativity the mass of any body increases when it is moving very rapidly. Ordinary things, trains, aeroplanes, etc.,

move far too slowly for this increase in mass to become significant; but for the very fast electron it becomes important.

If you consider a circular orbit, the electron is moving at a constant distance from the nucleus, its speed is constant and its mass is constant. But if the orbit is elliptical, the speed is different in different parts of the orbit, so the mass changes as the electron travels on its path. As the electron approaches the nucleus it moves faster and faster, so its mass increases. Owing to its heavier mass the electron is now less affected by the attractive force of the nucleus and it swings farther out from the nucleus. Each time the

electron approaches the nucleus it is swung round a little in this way ; it is as though the ellipse in which the electron moves were gradually rolling round the nucleus. The diagram shows the actual path of the electron.

(It is interesting to know that this forward roll of the orbit, known as precession, is quite considerable in the case of the planet Mercury, the planet which has the most elliptical orbit and which passes closest to the sun. This precession could not be explained by Newtonian mechanics ; the relativity theory offers a complete explanation.)

The importance of precession in the atom is that it has a slight effect on the energy of the atom. It is no longer true to say that the energy is the same for a circular orbit and for an elliptical orbit such that the semi-major axis of the ellipse is equal to the radius of the circle. There is a slight difference.

Now whenever the atom goes from one energy level to another a line appears in the spectrum corresponding to the transition. If there are two or more energy levels very close together, transitions to or from these levels will give rise to lines very close together in the spectrum. But this very condition is fulfilled if there are several elliptical orbits possible for the electron, in addition to a circular orbit. The energy of the atom is slightly different for each of the orbits, so we get several lines very close together in the spectrum. In fact, we get a fine structure.

The fine structure can be observed in the ordinary lines of hydrogen, the Balmer lines. It can be shown that these lines should each be split into three lines close together. Three lines cannot actually be observed, the most that can be seen is two, because the general blurring effect already mentioned makes the neighbouring fine lines merge into one another. But perfectly definite evidence has been obtained in the case of singly ionised helium, to which the theory is readily applied.

It is important to notice that only certain elliptical orbits are possible—the orbit cannot have all degrees of ellipticity. If it had, the line would merely be broadened, not split into two or more separate lines.

We can describe all the possible orbits in terms of two quantum numbers. The first we have met already. It is the principal quantum number n , and it determines the semi-major axis of the orbit. The second quantum number is known as the azimuthal quantum number and is represented by l . It determines how much the orbit is drawn out into an ellipse: when l is one less than n the orbit is circular; when l is two less the orbit is elliptical; when l is three less the orbit is more elliptical; and so on. l is always less than n , and it can never be less than 0. If it were -1 , for example, the orbit would be reduced to a straight line

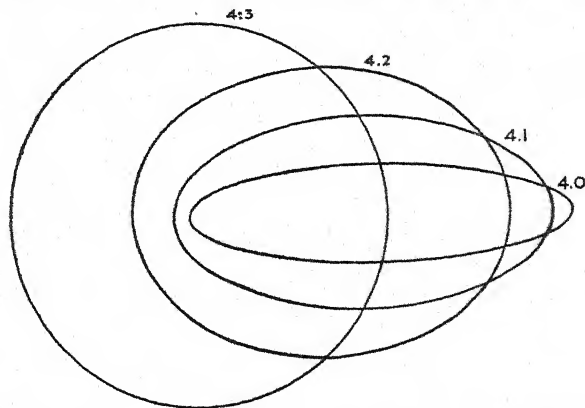


FIG. 8.—Elliptical orbits in the hydrogen atom. The principal quantum number, n , is 4 in each case; the azimuthal quantum number has values 3 to 0.

through the nucleus. Hence l can have any integral value from 0 to $n - 1$ inclusive, and no value beyond these limits.

As we have seen, n determines the energy of the atom for a particular orbit, and l introduces a small correction factor to this energy.

To describe completely an electron in an atom, we require two more quantum numbers. The two we have already met give us the size and shape of the orbit of the electron; we need to know also how the orbit lies in space, and in which direction the electron is spinning on its axis.

The third quantum number is called the magnetic quantum number, and is represented by m . It is concerned with the

position in space of the electronic orbit. It was actually introduced to account for the Stark and Zeeman effects in the spectrum. When a substance being examined spectroscopically is subjected to an electric field the lines are split up into two or more components equally spaced about the position of the original line; this is the Stark effect. The Zeeman effect is a similar effect due to a magnetic field. The magnetic quantum number is able to account for these effects, although the full theory is rather difficult. It transpires that m can have any integral value from $-l$ to $+l$ inclusive. Thus if l happens to be 3, m can have any of the values $-3, -2, -1, 0, 1, 2$ or 3 .

The spin quantum number, denoted by s , is introduced because the electron may spin on its axis. It may spin either in a clockwise or in an anti-clockwise direction, so the spin quantum number may have either of two values. It is usual to choose $+\frac{1}{2}$ and $-\frac{1}{2}$ for these two values; so that, when the spin of the electron changes, the change in s is unity.

We shall see in a later chapter that the four quantum numbers— n , l , m and s —are of great importance in discussing the electronic orbits of atoms more complex than the hydrogen atom.

CHAPTER V

THE SEQUENCE OF THE ELEMENTS

EVEN before the time of Mendeléev there had been many attempts to classify the elements, to group together elements of similar properties. For instance, it was seen that the elements calcium, strontium, and barium have certain properties in common. Their carbonates are all insoluble in water (calcium carbonate is familiar as chalk or limestone); their salts are most of them colourless in solution; and so on. It was noticed, too, that the properties of strontium usually fall in between those of calcium and barium. Calcium sulphate is not very soluble in water, whereas barium sulphate is one of the least soluble substances known; strontium sulphate is less soluble than calcium sulphate, but more so than the barium compound.

Most of these early attempts at classification merely grouped together a few elements with obvious resemblances in properties. Mendeléev's "periodic table" was far more comprehensive and included all the elements. His table stands to-day substantially in the form in which it was first published in 1869, and chemists learn it as the A B C of their subject.

Mendeléev arranged the elements in the order of their atomic weights, beginning with hydrogen, the lightest of the elements. He found that the series of elements can then be split up into "periods." The first element in each period resembles the first in every other period, the second resembles the second, and so on. Thus lithium, at the beginning of the "first short period," resembles sodium, at the beginning of the "second short period"; beryllium and magnesium, the second elements in these two periods, resemble one another; and so on.

The complete table is shown in Fig. 9. (This is a modern form of the table.) The periods are placed one under another,

The diagram shows the periodic table with elements arranged in columns and rows. The columns are labeled with group numbers (IA, IIA, etc.) and the rows with period numbers (I, II, etc.). The elements are connected by diagonal lines, indicating their periodicity. The elements are arranged in the following order from top to bottom:

Period 1: H, He

Period 2: Li, Be, B, C, N, O, F, Ne

Period 3: Na, Mg, Al, Si, P, S, Cl, Ar

Period 4: K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Kr

Period 5: Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Xe

Period 6: Cs, Ba, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Po, At, Rn

Period 7: Fr, Ra, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr

The diagram also includes labels for the Transition Elements (Sc to Zn, Y to Cd, etc.) and the RARE EARTHS (La to Lu, Ac to Lr).

FIG. 9.—Periodic Table of the Elements, after Julius Thomson. From Sherwood Taylor's *Inorganic and Theoretical Chemistry* (Heinemann).

so that sodium falls under lithium, magnesium under beryllium, and so on. Thus similar elements fall in vertical groups in the table. The alkali metals—lithium, sodium, potassium, rubidium, and caesium—form the first of these

groups; the elements beryllium, magnesium, calcium, strontium, barium, and radium form the second group; and so on across the table.

In this way we get a sort of double classification of the elements: a classification into "groups," reading down the table; and a classification into "periods," reading across the table. There is a regular gradation of properties as we go down a group or across a period.

The groups contain the more striking sequences in properties. We may take the group of the halogens as an example; it is the last group but one to the right of the table. Three properties of this group of elements are tabulated below, in order to exhibit the gradation in properties. It will be seen that the boiling-point rises steadily, the colour becomes more intense, and the reaction with hydrogen less vigorous, as we go down the group.

Element.	Boiling-point.	Colour.	Reaction with Hydrogen.*
Fluorine	-187° C.	Pale greenish yellow.	Explodes even in the dark.
Chlorine	-34° C.	Deeper yellowish green.	Explodes in the light.
Bromine	59° C.	Deep red.	Combines on heating.
Iodine	184° C.	Deep violet.	The reaction is definitely incomplete, even at low temperatures.

* All the halogens form compounds with hydrogen; these compounds are of the type HX where X stands for a halogen atom.

The gradation of properties in the periods is by no means so clear or definite as that in the groups, but there is no doubt that such a gradation does exist as well as a balance about the middle of each period. The first period contains but two elements, hydrogen and helium; so we will take the next period, from lithium to neon, as an example. Typical properties of the eight elements of this period are shown in the following table:

Element.	Melting-point.		Compound with Oxygen.	Compound with Chlorine.
Lithium	186° C.	} Metals.	Li ₂ O	LiCl
Beryllium	1400° C.		BeO	BeCl ₂
Boron	2000–2500° C.	} Non-metals ; probably giant mole- cules.	B ₂ O ₃	BCl ₃
Carbon			CO ₂	CCl ₄
Nitrogen	–210° C.	} Non-metals ; gases at ordinary temperatures.	N ₂ O ₅	NCl ₃
Oxygen	–219° C.		—	OCℓ ₂ *
Fluorine	–223° C.		F ₂ O	FCℓ*
Neon	–250° C.		Inert gas—forms no compounds.	

* Usually written Cl₂O and ClF.

The sequence in the case of the oxygen compounds can be seen more clearly if we double the formulæ BeO and CO₂. The series then becomes :



This brings out the sequence 1, 2, 3, 4, 5. The oxide of fluorine, F₂O, is anomalous as far as this sequence is concerned. In the compounds with chlorine, the sequence is 1, 2, 3, 4, 3, 2, 1, with a balance about the middle element.

The periodic table, as we now have it, contains hydrogen and helium by themselves at the beginning, and then the "first short period" from lithium to neon. There are eight elements in this period. The second short period also contains eight elements, from sodium to argon. These elements correspond to the elements in the first short period: sodium to lithium, magnesium to beryllium, and so on.

Next comes the first long period, which includes eighteen elements, from potassium to krypton. Potassium, the first element in this period, corresponds to lithium and sodium, the first elements in the previous periods. Calcium, the second element in this period, has resemblances to beryllium and magnesium. But after this the similarities begin to become less and less pronounced. Scandium resembles aluminium, titanium to a lesser extent resembles silicon, and so on; and by the time we reach manganese and

chlorine, the resemblances that do exist we should be inclined to ascribe to coincidence. The next three elements—iron, cobalt, and nickel—have no analogues at all in the two short periods. Then we come to copper. Copper does show faint resemblances to sodium; and when we come to the next pair, zinc and magnesium, the resemblances are more definite still. From now on the similarities between the elements in the first long period and those above them in the short periods become more and more noticeable; until eventually we reach the very similar pairs, bromine and chlorine, krypton and neon.

The series of elements from scandium to nickel are called transition elements; they are enclosed in a frame in Fig. 9.

The second long period also includes eighteen elements, from rubidium to xenon. The behaviour of the elements in this period is very much like that of those in the previous period. In particular, there is a series of transition elements, from yttrium to palladium. Yttrium has analogies to scandium, zirconium has analogies to titanium, and so on.

The third long period includes thirty-two elements, from caesium to emanation. The first two elements, caesium and barium, link up with the elements of the previous periods. Then comes a long series of twenty-two transition elements. The first fifteen of these form the group of elements known as the rare earths, and they are all remarkably similar in properties; yttrium, in the previous period, is also included in the rare-earth group of elements. After this series we find seven more transition elements, corresponding to the transition elements of the two previous periods: hafnium resembles zirconium, and so on. The period then finishes off in the same manner as does the previous period.

Beyond the third long period is the beginning of another period. The elements in this period are all unstable, radioactive.

Mendeléev arranged the elements in the order of their atomic weights. It was found necessary to interchange the order of three pairs of elements; their properties indicated that they should be placed in the opposite order to that indicated by their atomic weights. The three pairs are:

argon and potassium, cobalt and nickel, iodine and tellurium. At first it was thought that there was a small error in the determinations of the atomic weights of these elements, but it is now known that they represent genuine anomalies.

The discovery of the atomic numbers by Moseley cleared up these anomalies and placed the whole table on a more rational basis. The atomic number, the number of positive charges on the nucleus, is what is really characteristic of the element, rather than its atomic weight. The atomic number increases steadily, one by one, from element to element, whereas the atomic weight increases rather haphazardly. This makes us feel confident in arranging the elements in the order of their atomic numbers, instead of in the order of their atomic weights. The two orders are the same, except for the three anomalous pairs of elements; and when arranged in the order of their atomic numbers the elements of these pairs fall in the positions to which they had previously been allocated on chemical grounds.

	Atomic Numbers.	Atomic Weights.
{ Argon	18	39.944
{ Potassium	19	39.096
{ Cobalt. . . .	27	58.94
{ Nickel. . . .	28	58.69
{ Tellurium	52	127.61
{ Iodine. . . .	53	126.92

The discovery of the isotopic constitution of the elements has shown why the atomic weights of these pairs of elements fall in the wrong order. We may take the pair argon and potassium as an example. Argon consists of isotopes of masses 36 and 40, and potassium of isotopes of masses 39 and 41. It so happens that the heavier isotope of argon, A^{40} , and the lighter isotope of potassium, K^{39} , are the predominating isotopes in the two cases. Thus the atomic weight of potassium turns out to be less than that of argon.

THE DISCOVERY OF NEW ELEMENTS.—Mendeléev found it necessary to leave a number of gaps in his table for

elements then undiscovered. Now the properties of any element depend on its position in the table, so Mendeléev was able to predict the properties of these unknown elements. His predictions were verified in a remarkable manner in several instances. The properties of gallium, a metal of the boron-aluminium group, were predicted by Mendeléev in 1871, and the element was actually discovered in 1875. The table of predicted and actual properties affords a convincing proof of the fundamental truth of the periodic table :

Mendeléev's Predictions.	Actual Properties.
Atomic weight, about 69. Low melting-point. Specific gravity, about 5.9. Not acted on by air.	Atomic weight, 69.72. Melting-point, 29.7° C. Specific gravity, 5.90. Very slightly oxidised by air at a red heat.
Will decompose water at a red heat. Oxide Ga_2O_3 ; chloride GaCl_3 ; sulphate $\text{Ga}_2(\text{SO}_4)_3$. Probably more volatile than aluminium; hence its discovery by the spectroscope is likely.	Decomposes water at high temperatures. As predicted. Recognised by the brilliant violet lines in its spectrum.

Before the discovery of atomic numbers it was impossible to say definitely how many gaps should be left in the periodic table. When the atomic numbers had been discovered it was possible, for the first time, to call the roll of the elements; gaps were readily detected in the steady, one by one progression of the atomic numbers.

By 1920 all the elements except six had been discovered, apart from the possibility of elements beyond number 92. These six occupied the following places in the periodic table: 43, 61, 72, 75, 85, and 87. There was no doubt that elements should exist to fill these places; but did they exist in detectable quantities?

As has been pointed out, it was possible to make a fairly

accurate prediction of their properties ; so it was known what minerals would be most likely to contain these elements.

The most hopeful method of search was by means of X-ray spectra. The special advantage of this method is that the positions of the lines in X-ray spectra can be calculated from the atomic numbers of the elements ; one knows, therefore, exactly where to look for the lines in the case of any particular element. Moreover, the method is a sensitive one ; very small quantities of an element can be detected in this way. There is, however, the disadvantage that, knowing exactly where to look for the lines, one may be deceived into thinking they are present in faint traces even when they are entirely absent ; it is not wise to trust the eye of faith too far.

The first of the six elements to be discovered was number 72. This element belongs to the same group as zirconium, which is in the period above. It was originally supposed that it would turn out to be another rare earth ; but Bohr predicted that it would have properties similar to those of zirconium, and might occur along with zirconium in minerals. Coster and Hevesy accordingly examined the X-ray spectra of various minerals containing zirconium ; in 1923 they discovered the element and named it hafnium (Hf). Some zirconium minerals contained surprisingly high percentages of hafnium, in one case as much as 30 per cent. In spite of these quite large quantities the element had previously escaped detection because of its exceptionally close resemblance to zirconium. Hafnium has now been isolated in sufficient quantities to enable its chemical and physical properties to be conveniently determined.

Elements 43 and 75 fall in the same group as manganese. They were sought for in minerals containing elements close to them in the table ; both were detected by their X-ray spectra. Element 43 was given the name masurium (Ma) and element 75 the name rhenium (Re). Rhenium has since been isolated in fairly large quantities and is available commercially ; masurium has, however, gone the way of many new elements—no further proof of

its existence has been advanced and there seems to be no further interest in it.

Element 61 falls in the group of the rare earths. There are fifteen of these elements, and they show a slow progressive change in properties, so that it is not easy to distinguish one from another. Element 61 has been recognised and named illinium (Il); but the recognition is doubtful as it might so easily be confused with other rare earth elements. It is possible that illinium may be radioactive. Its nearest relative amongst the elements is samarium, element 60. It has been claimed that samarium is radioactive; this may in reality be due to the presence of a certain amount of illinium in the samarium preparations examined. If illinium *is* radioactive it may have nearly all disintegrated; this would explain why there is so little of it in nature.

Elements 85 and 87 may also be radioactive, and they, too, may have nearly all disintegrated away so that only faint traces are left—mere ghosts of departed elements. The two elements have been sought for by examining the X-ray spectra of preparations of closely related elements; they might be present as impurities. From the position of element 87 in the table we know that it is the last of the alkali metals; caesium is the last but one. Minerals containing caesium were, therefore, worked up for their caesium content. It was expected that element 87 would concentrate along with the caesium on account of the anticipated similarity in properties between these two elements. In 1931 10 kilogrammes of samarskite was examined. Samarskite is a rare earth mineral rich in uranium and other radioactive elements; this specimen contained noteworthy quantities of rubidium and caesium as well. So there was the double chance that element 87 might occur along with its nearest relative, caesium, or along with the other radioactive elements. The mineral was worked up for caesium, and the X-ray spectra of the concentrate indicated the presence of element 87. There is also evidence from other sources for the existence of this element.

Until 1934 there was no evidence of the existence of any

elements with a higher atomic number than 92 (uranium). In 1934 Fermi bombarded uranium with neutrons. It may be remembered that the nuclei formed by the bombardment are unstable. The unstable nuclei decay at a definite rate, and this rate can be used to characterise the element. When uranium is bombarded a whole series of unstable products is formed, each one with its characteristic rate of decay. We can investigate, indirectly, the chemical properties of each of the products, and so find where to put them in the periodic table; in other words, we find their atomic numbers. It seems that one of the products must have an atomic number of 93 (or possibly 94 or 95). So it is at least one place beyond uranium.

THE BOHR THEORY AND THE PERIODIC TABLE.—The Bohr theory cannot be applied in an exact manner to the discussion of any of the elements except hydrogen (and He^+ and Li^{++}). Nevertheless, it can be applied in a semi-quantitative way to the discussion of the periodic table.

Before beginning this discussion it may be well to summarise the properties of the four quantum numbers which describe the orbits of the electrons.

The principal quantum number, denoted by n , can be any whole number: 1, 2, 3, etc.

The azimuthal quantum number, denoted by l , can be any whole number from 0 up to one less than n . Thus, when $n = 3$, l may be 0, 1, or 2.

When n and l are fixed, the magnetic quantum number, m , may be any whole number from $-l$ to $+l$. Thus, when $n = 4$, l may be 0, 1, 2, or 3. Suppose in a particular case $l = 3$, then m can have any of the values $-3, -2, -1, 0, 1, 2$ or 3 .

In every case the spin quantum number, s , may be either $+\frac{1}{2}$ or $-\frac{1}{2}$.

There is one other principle necessary before the orbits can be sorted out. This principle is known as Pauli's exclusion principle; it arose originally in spectroscopic investigations. *No two electrons in an atom can have all four quantum numbers alike.*

We will now apply these simple ideas to the electronic orbits.

The principal quantum number, n , gives us the size of the orbit. [Actually the semi-major axis is proportional to n^2 .] Hence we get a series of groups or "shells" of orbits of increasing size—those for which $n = 1$, those for which $n = 2$, and so on.

Orbits for which $n = 1$. l can only be 0 (since it is less than n). m (any whole number from $+l$ to $-l$) must also be 0.

The only variable is s , which can be $+\frac{1}{2}$ or $-\frac{1}{2}$ in every case. Hence only two orbits are possible, those for which:—

$$\begin{aligned} n = 1, l = 0, m = 0, s = +\frac{1}{2} \\ n = 1, l = 0, m = 0, s = -\frac{1}{2} \end{aligned}$$

Orbits for which $n = 2$. $l = 0$ or 1 . When $l = 0$, $m = 0$; when $l = 1$, $m = -1, 0$, or 1 . $s = \pm \frac{1}{2}$ in every case.

The possible orbits are those for which:

$$\begin{aligned} & \left. \begin{aligned} n = 2, l = 0, m = 0, s = +\frac{1}{2} \\ n = 2, l = 0, m = 0, s = -\frac{1}{2} \end{aligned} \right\} \text{1st subgroup.} \\ & \left. \begin{aligned} n = 2, l = 1, m = -1, s = +\frac{1}{2} \\ n = 2, l = 1, m = -1, s = -\frac{1}{2} \\ n = 2, l = 1, m = 0, s = +\frac{1}{2} \\ n = 2, l = 1, m = 0, s = -\frac{1}{2} \\ n = 2, l = 1, m = 1, s = +\frac{1}{2} \\ n = 2, l = 1, m = 1, s = -\frac{1}{2} \end{aligned} \right\} \text{2nd subgroup.} \end{aligned}$$

The eight orbits of the second shell are divided into two subgroups: the two orbits for which $l = 0$, and the six orbits for which $l = 1$.

There is no need to go through all the shells in detail, but the following summaries are useful:

Orbits for which $n = 3$.

Subgroups—

$$\begin{aligned} & \left. \begin{aligned} l = 0, m = 0 \\ l = 1, m = -1, 0, \text{ or } 1 \\ l = 2, m = -2, -1, 0, 1, \text{ or } 2 \end{aligned} \right\} \begin{array}{ll} s = \pm \frac{1}{2} & 2 \text{ orbits} \\ \text{throughout} & 6 \text{ " } \\ & 10 \text{ " } \\ & 18 \text{ " } \end{array} \end{aligned}$$

This gives 18 orbits in all.

Orbits for which $n = 4$.

Subgroups—

$l = 0, m = 0$	$\left\{ \begin{array}{l} s = \pm \frac{1}{2} \\ \text{throughout} \end{array} \right.$	2 orbits
$l = 1, m = -1, 0, \text{ or } 1$		6 "
$l = 2, m = -2, -1, 0, 1, \text{ or } 2$		10 "
$l = 3, m = -3, -2, -1, 0, 1,$ 2, or 3		14 "
		—
		32 "
		—

This gives 32 orbits in all.

A little reflection will show that the numbers of values of m in the subgroups follow the sequence of odd numbers: 1, 3, 5, 7 . . . The numbers of orbits in the subgroups are, therefore, 2, 6, 10, 14 . . . This accounts for the fact that the total number of orbits in any shell is twice a square number. [$1 = 1^2$; $1 + 3 = 2^2$; $1 + 3 + 5 = 3^2$; $1 + 3 + 5 + 7 = 4^2$; and so on. These numbers are doubled because of the two values of s in every case.]

The sequence of the elements can now be described in greater detail.

The nucleus of every atom has a positive charge, and this charge increases by one unit as we go from element to element throughout the table. In a neutral atom the positive charge on the nucleus is exactly balanced by the negative charges of the electrons. Hence we know that the number of electrons also increases one by one as we go from element to element.

In a hydrogen atom there is one electron revolving in a very small orbit about the nucleus. The orbit has the quantum numbers:

$$n = 1, l = 0, m = 0, s = \pm \frac{1}{2}$$

The value $n = 1$ shows that it is the smallest of the orbits; $l = 0$ shows that it is circular. In a particular case, s may be either $+\frac{1}{2}$ or $-\frac{1}{2}$, that is, the electron may rotate either in a clockwise or an anti-clockwise direction.

(It is to be understood in every case throughout this discussion that the atom is supposed to be in its ground state. When it is excited the electrons jump to higher orbits.)

204389 E 2

5410
408

The helium atom has two electrons which revolve in orbits for which :

$$\begin{aligned} n = 1, l = 0, m = 0, s = +\frac{1}{2} \\ n = 1, l = 0, m = 0, s = -\frac{1}{2} \end{aligned}$$

Both these orbits are filled—not merely one or the other, as in the case of hydrogen. In helium, therefore, the innermost shell of orbits is completely filled ; any further electrons in this shell would have to duplicate one of the sets of quantum numbers of the electrons already there, and this is forbidden by the Pauli exclusion principle. The structure of the helium atom is often written (2), which means that the two orbits in the first shell are filled up. (When the “structure” or “configuration” of an atom is referred to

in this way, it is always the arrangement of its electrons that is implied.)

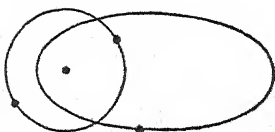


FIG. 10.—The orbits of the electrons in the lithium atom.

Lithium has three electrons revolving round the nucleus. Two have orbits with the same sets of quantum numbers as the helium electrons. The third must start a second shell of orbits farther out,

the shell for which $n = 2$; it cannot enter the first shell without violating the Pauli principle. It goes into one of the two orbits for which :

$$n = 2, l = 0, m = 0, s = \pm \frac{1}{2}$$

(In a particular lithium atom, s may be either $+\frac{1}{2}$ or $-\frac{1}{2}$.) The electrons generally fill up the $l = 0$ subgroups first, the $l = 1$ subgroups next, and so on. Thus the most elliptical orbits are filled first, and the circular orbits (for which l is one less than n) are filled last. Lithium has, then, two electrons in the first shell, and one electron in an elliptical orbit in the second shell ; the orbit of the electron in the second shell carries it a long way off from the nucleus during part of its path, so that it is particularly easy to remove from the atom. The structure of lithium is (2) (1). This indicates that the two orbits of the first shell and one orbit of the second shell are filled.

Beryllium has four electrons in the four lowest possible orbits, those for which :

$$n = 1, l = 0, m = 0, s = +\frac{1}{2}$$

$$n = 1, l = 0, m = 0, s = -\frac{1}{2}$$

$$n = 2, l = 0, m = 0, s = +\frac{1}{2}$$

$$n = 2, l = 0, m = 0, s = -\frac{1}{2}$$

The first subgroup in the second shell is now full. The next electron goes into the subgroup for which $l = 1$. This subgroup fills up, orbit by orbit, until six elements later it is completely filled. We have reached neon, another inert gas, with the first two shells of orbits filled. The structure of neon is (2) (8), or, if we wish to indicate the subgroups, (2) (2, 6).

It will be seen that each shell of orbits corresponds to a period in the periodic table, and that an inert gas without any incomplete shells ends each period.

The third group of orbits, for which $n = 3$, starts with sodium which has one electron more than neon. The extra electron goes into the lowest subgroup, that for which $l = 0$; this is again the most elliptical orbit. The outer electron is particularly easy to remove (like the outer electron of lithium) because of the elongation of its orbit; in one part of the orbit the electron is a long way from the nucleus. Sodium has the structure (2) (8) (1) or (2) (2, 6) (1).

The first and second subgroups of the third shell are next filled up, orbit by orbit. This brings us to argon, an inert gas, which has the structure (2) (8) (8) or (2) (2, 6) (2, 6). It might be expected that the ten orbits of the third subgroup would now fill up. But this is not so; the next electron goes into the group for which $n = 4$. And so it occurs that argon ends the second short period of elements.

The element following argon is the alkali metal potassium. The additional electron for this element goes into the lowest orbit of the shell for which $n = 4$. (Its structure is (2) (8) (8) (1).) The reason for this behaviour is that the electrons in the third shell are becoming too crowded. Each electron has a negative charge, and they are all, therefore, repelling

each other. The mutual repulsions between them are so strong that the positive charge on the nucleus can no longer constrain them. The additional electron is driven into the fourth shell by these repulsions. Hence we get potassium with one easily removable electron in the most elliptical orbit of the fourth shell. This element begins the first long period.

The next electron also is driven into the fourth shell, giving calcium, with two easily removable electrons, and the structure (2) (8) (8) (2).

The two electrons thus driven into the fourth shell form a protective sheath as it were. They exert repulsions against any electron trying to invade the fourth shell. The repulsions of these two electrons enable the next electron to go into the third shell of orbits in spite of the repulsions of the eight electrons already there. This gives scandium, with the structure (2) (8) (9) (2) or (2) (2, 6) (2, 6, 1) (2).

We come here to an extremely interesting point about the scandium ion. (The scandium ion is a scandium atom with three positive charges; the charges are due to the loss of three electrons. The ion is represented by Sc^{+++} .) When the atom is ionised, obviously the two outer electrons are lost first; this gives the structure (2) (8) (9) with a net positive charge of two units, due to the loss of two electrons. But it was just those two outer electrons that enabled the third shell to hold an extra electron. As soon as they are gone this extra electron is given up too, and we are left with the argon structure (2) (8) (8) with a net positive charge of three. This is the scandium ion Sc^{+++} .

Beginning with scandium and continuing as far as nickel, there is a possibility of the extra electrons going into either the third or fourth shell; in each case the matter is decided in favour of the arrangement which requires least energy. These elements have the following structures when they are in the metallic state:

scandium (Sc) . . .	(2) (8) (9) (2)
titanium (Ti) . . .	(2) (8) (10) (2)
vanadium (V) . . .	(2) (8) (11) (2)
chromium (Cr) . . .	(2) (8) (13) (1)

manganese (Mn)	.	.	(2) (8) (13) (2)
iron (Fe)	.	.	(2) (8) (14) (2)
cobalt (Co)	.	.	(2) (8) (15) (2)
nickel (Ni)	.	.	(2) (8) (16) (2)
[copper (Cu)	.	.	(2) (8) (18) (1)]

In all these metals (scandium to nickel) the electrons can pass between the outermost shell and the shell immediately below. For this reason they are often called "transition elements" (or sometimes "transition elements in the wider sense," because the term used to be applied only to iron, cobalt, nickel, and the other elements in the eighth group of the periodic table).

Copper is the first element to have the third shell of orbits completely filled. The fourth shell then fills up, orbit by orbit, until the first two subgroups are complete. This brings us to the inert gas krypton with the structure (2) (8) (18) (8). This ends the first long period of elements.

Rubidium starts the second long period with one electron in the fifth shell and the structure (2) (8) (18) (8) (1). The inert gas xenon ends this period; as usual it has the first two subgroups in the final group complete: (2) (8) (18) (18) (8).

Cæsium starts the third long period with one electron in the sixth shell and the structure (2) (8) (18) (18) (8) (1). Emanation, an inert gas produced during the disintegration of radioactive elements, ends the period; it has the structure (2) (8) (18) (32) (18) (8). It has the first four shells of orbits complete and the next two as complete as they can be when the seventh shell is empty.

The elements beyond emanation form the sketchy beginning of another long period. They are all radioactive and unstable (except perhaps element 87). Each has at least one electron in the seventh shell of orbits. Uranium (element 92), which ends the table, has the structure (2) (8) (18) (32) (18) (13) (1). A truly cumbrous system of satellite electrons!

It will have been noted that each period of the table of elements ends with an inert gas. In each of these gases the inner shells of orbits are completely filled and the outer-

most shell contains eight electrons (except, of course, in the case of helium). This sort of structure is evidently a very stable one. The inert gases are chemically inactive, they form no compounds (except under extraordinary conditions). In the matter of electrons they appear to be sated. It will be seen later that other elements tend toward these structures.

CHAPTER VI

CHEMICAL LINKS

It has already been noted that each period in the periodic table of the elements ends with an inert gas, and that each of these has a very stable arrangement of the electrons, with eight electrons in the outermost group of orbits (except for helium, which has two). The structures of these gases are given here, as they will be needed in this chapter. The structures are often referred to as "inert gas configurations." They are :

helium (He)	.	.	(2)
neon (Ne)	.	.	(2) (8)
argon (A)	.	.	(2) (8) (8)
krypton (Kr)	.	.	(2) (8) (18) (8)
xenon (Xe)	.	.	(2) (8) (18) (18) (8)
emanation (Em)	.	.	(2) (8) (18) (32) (18) (8)

When we come to consider the chemical properties of the elements we find that they are associated with the outer layers of electrons. Similarity in these outer layers goes along with similarity of chemical properties. Each member of the group of alkali metals (lithium, sodium, potassium, rubidium, caesium, element 87) has a single electron in the outermost shell of orbits. This similarity of structure is associated with a similarity of chemical properties, which has led to these elements being grouped together.

We will take sodium as an example of an alkali metal. It is the first element to have an electron in the third shell of orbits ; its structure is (2) (8) (1). Now if the sodium atom were to lose the single electron in the outermost shell it would be reduced to the stable structure of neon, (2) (8). It would not, of course, *be* neon ; its atomic number would be eleven, not ten as with neon, because the charge on the nucleus has not been changed. In losing the electron, the

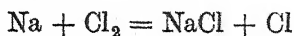
sodium atom has lost a negative charge. This is equivalent to gaining a positive charge. The sodium atom has thus become an ion ; it is represented by Na^+ , where the plus sign indicates that the charge on the ion is positive. Whenever the conditions are suitable a sodium atom will always give up an electron and become a positive ion, with the stable neon structure.

Indeed metallic sodium does not consist of neutral sodium atoms, but of positive sodium ions floating in a sea of electrons.

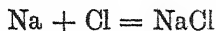
At the other end of the second short period of elements is chlorine, with the configuration (2) (8) (7). The gain of a single electron would give the chlorine atom the stable argon structure (2) (8) (8). It would become a chloride ion, with a negative charge, because of the additional electron. This ion is represented by Cl^- .

When sodium and chlorine atoms meet, the sodium atom is anxious to give up an electron and become a positive ion ; the chlorine atom is equally anxious to gain an electron and become a negative ion. There is an instant reaction. The electron is exchanged ; the two atoms become ions with opposite charges. From that moment they are held together by electrostatic attraction, the attraction that unlike charges have for each other.

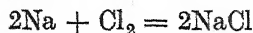
The reaction between metallic sodium and chlorine gas is not quite so simple as this. The chlorine exists as molecules and the first reaction is :



This is followed by :



The double reaction is equivalent to :

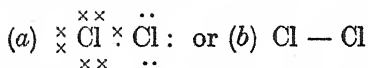


In such a way is a molecule of common salt produced. The force holding the atoms together in the molecule is the attraction between oppositely charged ions. Compounds formed in this way are called ionised compounds, and the links between the atoms are called ionised or electrovalent links.

When two chlorine atoms meet, a different sort of compound is formed. Each atom of chlorine has seven electrons in its outermost shell ; it is one short of the number of electrons required to complete the stable argon configuration (2) (8) (8). By what trick of mathematical jugglery can two sevens be made to yield two eights ? The impossible is achieved by each atom donating an electron toward a common link. Each atom shares the two electrons of the link, and so completes its octet of outer electrons. The electrons are not surrendered by either atom ; they are both closely associated with each atom, and thus constitute a link which holds the two atoms together as a molecule. This link is called the covalent link.

In this way arises the molecule of chlorine, Cl_2 , which consists of two atoms of chlorine held together by a covalent link of two electrons, one supplied by each atom. The necessity of linking up in this way is so urgent that solitary chlorine atoms are very rare.

The structure of the chlorine molecule is represented by :



These are two ways of representing exactly the same thing. The dots and crosses in (a) represent the outermost shells of electrons of the two chlorine atoms ; at the link one electron from each atom is shown. (The two symbols for the electrons are used merely to indicate to which atoms the electrons originally belonged. The electrons themselves are, of course, identical.)

In (b) the line indicates the covalent link of two electrons, one electron from each atom. This is what a line, used in this way, always means : a covalent link of two electrons, one from each of the atoms joined by it.

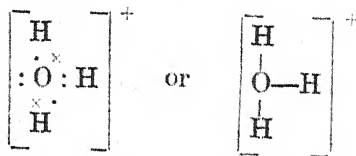
Thus there are two different kinds of link which can unite the atoms in a molecule :

(1) The ionised link, or the electrovalent link, is the electrostatic attraction between ions with opposite charges.

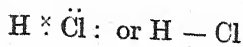
(2) The covalent link consists of two electrons, both of them held firmly by each of the linked atoms.

There is a possible objection to the term "ionised link," because it is not a link at all in the same sense as the covalent link, where the electrons are connected in some way with both atoms. The ionised link is merely an attraction.

Hydrogen is unique amongst the elements because of its single electron: it needs only one more electron to complete the outer shell and give it the inert gas structure of helium, (2). Thus hydrogen can give up its single electron and form ionised compounds in which it appears as the positive ion H^+ . [The H^+ ion rarely exists in this simple form, without any electrons at all. In ionising solvents the ions are solvated, that is each ion is attached to a molecule of the solvent. Each hydrogen ion in the solvated ion has the helium configuration. The hydrated ion, H_3O^+ , for example, is an H^+ molecule attached to a water molecule. Its structure may be represented by :



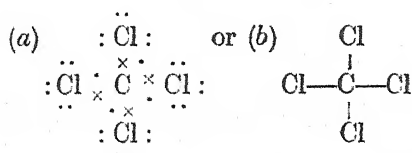
In all its compounds, whether ionised or covalent, the hydrogen atom has the helium configuration.] And it can also form covalent links with substances, like chlorine, which have seven electrons in the outermost shell. Thus it forms the compound hydrogen chloride, HCl . This is usually met with as an ionised compound (because it is ordinarily used in aqueous solution). In the un-ionised state the atoms of hydrogen chloride are united by a covalent link :



Because it can give up its single electron and form ionised compounds, hydrogen has resemblances to the alkali metals; like them it has one electron in the outermost shell. It also has resemblances to the halogens; like them it requires one electron to give it an inert gas structure.

We will now consider one or two molecules which are

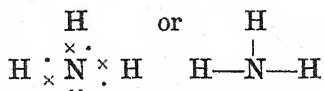
rather more elaborate than the simple cases just dealt with. Carbon has the structure (2) (4). It has four electrons in its outermost shell, so it can form links with four atoms—such as four chlorine atoms—which need one electron each to complete their outer octets. Thus an atom of carbon can unite with four atoms of chlorine to form a molecule of carbon tetrachloride, CCl_4 . This compound is represented by :



(Two ways of representing the same thing.)

In (a) the outermost octet of electrons is shown completed for each atom ; the dots represent those electrons which belonged originally to the chlorine atoms, the crosses represent the original four electrons in the outer shell of the carbon atom. In (b) each line represents a covalent link of two electrons, one supplied by the carbon atom and the other by one of the chlorine atoms. Carbon tetrachloride has a stable structure ; each atom has its complete octet of outer electrons. It is saturated, and enters into very few reactions. Indeed this is the reason why it can be used as a fire extinguisher ; it prevents oxygen getting at the burning material.

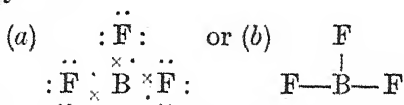
Nitrogen has the structure (2) (5). It reacts with hydrogen to form ammonia, thus :



The three hydrogen atoms are saturated ; each has the two electrons necessary to give it the inert gas configuration, He (2). The nitrogen atom also is saturated, but it has two spare electrons in its outer group, two which are not shared with another atom (as, for example, the other electrons are shared with the hydrogen atoms). The two spare electrons are sometimes called a "lone pair," and sometimes an

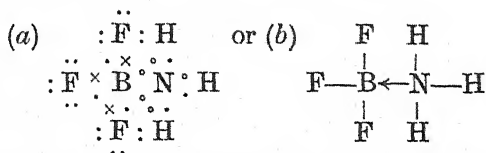
"unshared pair." Now the lone pair of the nitrogen atom can itself form a complete covalent link with another atom or group; the nitrogen atom supplies both the electrons of the link. For this reason ammonia can react with other atoms or molecules, although it is itself apparently a saturated compound, each atom having an inert gas configuration.

Ammonia can, for example, combine with boron trifluoride, BF_3 . The latter substance is a colourless gas which fumes in moist air, and thus shows that it is fairly reactive. It is an example of a compound in which one of the atoms has not got an inert gas configuration. The structure of boron is (2) (3) and of fluorine (2) (7). The compound may be represented by :



From (a) it may be seen that each fluorine atom has its complete octet of outer electrons. The boron atom, however, has only six outer electrons.

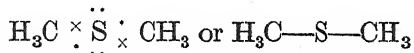
In ammonia and boron trifluoride we have the conditions for combination to take place: the nitrogen atom in ammonia has a lone pair, and the boron atom in boron trifluoride is short of two electrons to complete its outer octet. The two substances react thus :



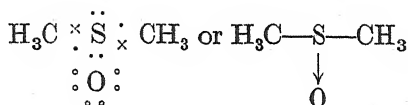
In (a) the two electrons in the link between the boron and nitrogen atoms are clearly shown as both coming from the nitrogen atom. Such a link, in which both atoms come from the same atom, is called a co-ordinate link. In (b) the co-ordinate link is indicated by an arrow. The direction of the arrow shows that both electrons in this case are supplied by the nitrogen atom. [The arrow also shows that the negative charges of the two electrons in the co-ordinate

link are moved toward the boron atom. Thus there is a net negative charge toward the boron side and a net positive charge toward the nitrogen side; the molecule has a considerable polarity. For this reason the co-ordinate link is sometimes called the semi-polar link. *Semi-polar*, to distinguish this case from the more definite polarisation in ionised compounds.]

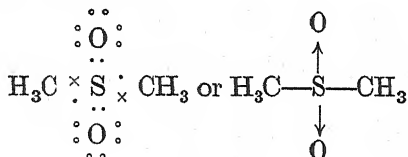
Dimethyl sulphide, $(\text{CH}_3)_2\text{S}$, is an example of a compound with two lone pairs. Its structure is :



(In the CH_3 groups three of the four carbon electrons form covalent links with hydrogen atoms, leaving the carbon atom in each case a single electron to form a link with the sulphur atom.) One of the lone pairs of the sulphur atom can form a co-ordinate link with an oxygen atom, giving dimethyl sulphoxide :



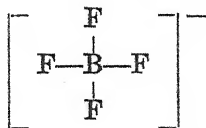
Or both of the lone pairs may form co-ordinate links, giving dimethyl sulphone :



Lone pairs have not all equal facility in forming co-ordinate links. In some cases such links are formed very readily, and in other cases with great difficulty.

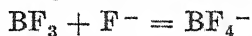
Ions as well as neutral molecules can form co-ordinate links. A fluoride ion, F^- , for example, has four lone pairs, and can form a co-ordinate link with boron trifluoride, BF_3 . The link, once it has been formed, is just like the other links between the boron and the fluorine atoms: it consists of two electrons. We then have the BF_4^- ion; the negative charge, indicated by the minus sign, is not attached

specially to any one of the atoms, but is connected with the BF_4 group as a whole. The BF_4^- ion is, therefore, represented by



These negative ions cannot exist in quantity unless there are balancing positive ions, such as the potassium ion, K^+ , present too.

Now see how this can come about. Boron trifluoride reacts with potassium fluoride, KF . The latter is an ionised compound; the ions are K^+ and F^- . The fluoride ion, F^- , is just what BF_3 needs for the boron atom to complete its octet; the two react to form the BF_4^- ion. We thus have the K^+ ion and the BF_4^- ion forming an ionised compound called potassium fluoborate. The potassium ion, as it were, keeps the ring clear for the reaction:



(This is the actual reaction, and not, as usually written: $\text{BF}_3 + \text{KF} = \text{KBF}_4$.) The formula for potassium fluoborate is written $\text{K}[\text{BF}_4]$ or $\text{K}\{\text{BF}_4\}$. The brackets are used to indicate that BF_4 is an ion.

CHAPTER VII

GIANT MOLECULES

THE covalent links between the atoms in a molecule are usually much stronger than the forces between different molecules. It is comparatively easy to separate molecule from molecule : for example we can separate the molecules of a liquid by simply vaporizing it. It is generally a much more difficult thing to separate the atoms linked together in a molecule (although, of course, there are substances which are more easily decomposed than vaporized).

In most crystals the molecules are extremely minute. The ease with which they can be separated depends on the strength of the forces between them : in a substance like sodium chloride there are powerful forces between the oppositely charged sodium and chloride ions, so it is relatively difficult to separate them ; but in most organic compounds the forces between the molecules are comparatively weak. Thus the molecules of such substances can be separated fairly easily by solution or vaporization.

The diamond is particularly difficult to dissolve or vaporize, so its atoms are evidently held together by unusually powerful forces. A white diamond consists of pure carbon and nothing else, not even the faint traces of colouring matter that tint other diamonds. The atoms of carbon in a diamond are held together by an exceptional system of covalent links, and it is this that gives the diamond its remarkable properties.

Each atom in a diamond is covalently linked to four other carbon atoms. These atoms are arranged symmetrically round the central one, at the four corners of a tetrahedron. Each atom in turn is linked in this way ; so that the system of links extends in all directions throughout the diamond.

Every atom in a diamond is thus held by four powerful

links to four other atoms. A diamond is, in fact, a "giant molecule." Giant molecules differ from ordinary molecules only in the vast number of atoms they contain; a link between two carbon atoms in a diamond is essentially the same as the link between two carbon atoms in, say, alcohol. But the difference in the number of atoms between a giant molecule and an ordinary molecule is enormous: a small diamond may contain perhaps 10^{22} (10,000,000,000,000,000,000,000) atoms, whereas even a complex organic molecule like starch contains only a few thousands of molecules. One result of this is

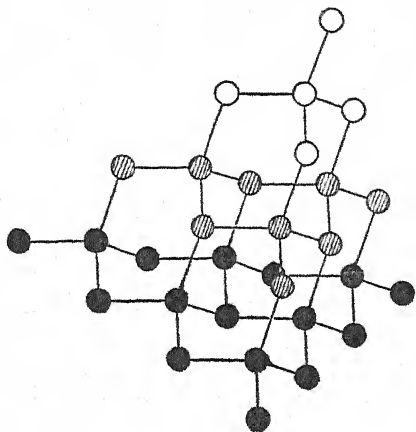


Fig. 11.—The system of covalent links in diamond. The five unshaded atoms clearly form a tetrahedron. The shading of the other atoms shows how they are arranged in layers.

that each giant molecule—each diamond—is separately visible, whilst even the highest-power microscope will not show us the individual molecules in an ordinary organic compound.

The extreme hardness of the diamond is explained by the intensive chemical linking of the atoms. In the scale of hardness of materials the diamond is in a class apart, far harder than any other material; so that small diamonds in the cutting face of a drill give it an irresistible cutting power. Incidentally, the hardness of the diamond shows how strong covalent links can be.

The atoms of the diamond are so strongly linked that it cannot be melted or dissolved, and it is extremely difficult

to vaporize. To do any of these things to a diamond it would be necessary to break the covalent links ; not merely, as in most other cases, to separate molecule from molecule.

Graphite, like diamond, is composed of the single element carbon ; but could two substances be more different in properties ? The difference is explained by a different system of chemical links. In a diamond the links extend in every direction, so that the whole giant molecule is a single unit. In graphite the atoms are linked together in planes, producing a different kind of giant molecule—a two-dimensional rather than a three-dimensional one.

Imagine an extremely thin section of an extremely minute

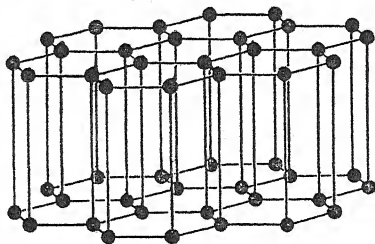


FIG. 12.—The covalent links in graphite.

honeycomb, with a carbon atom at each corner linked to the other carbon atoms about it. Graphite consists of such extremely thin layers, each one atom thick. The distance between the planes is very small, but it is actually more than twice as great as the distance between the atoms in the planes. [The distance between the atoms in the planes is 1.45×10^{-8} cm., and the distance between the planes is 3.41×10^{-8} cm. The distance between the atoms in the planes is very nearly the same as in diamond, where it is 1.54×10^{-8} cm.]

The method of linking helps to explain why graphite can be used for lubrication. The planes are not connected together by covalent links, so there is no strong connecting force between them ; they readily slip over one another.

The planes in graphite are not, of course, of very large

area, so graphite consists of a large number of minute platelets. These platelets are grouped into minute crystals, which are mixed up haphazard in ordinary graphite. A method has been found to orient the little platelets so that they are all parallel. Finely divided graphite is suspended in a warm solution of some substance like gelatin. Whilst the solution is still warm it is placed in a rotating electric field; this causes the platelets of graphite to set parallel to the field. The field is kept rotating while the solution cools and sets to a jelly, thus fixing the position of the platelets and preserving their orientation parallel to one another.

The result is surprising. Looking down from above we see the full area of each of the platelets and the graphite appears black as it usually does; but looking from the side we see the platelets edge-on and the graphite is all but invisible! Here is a new suggestion for an invisible man; visible only to birds and chance airmen.

Bakelite, a new toy of the manufacturer, is of the nature of a giant molecule, though it lacks the elegant symmetry of the diamond. The raw materials of bakelite are formaldehyde and various phenols. (The familiar germicide, formalin, is a 40 per cent. solution of formaldehyde in water. The phenols are a group of compounds of which carbolic acid—itsself called phenol—is the best-known member.) The formaldehyde is condensed with one or other of the phenols. The resulting substance is soluble in alcohol, and—more important from the manufacturer's point of view—it is fusible. In the fusible state bakelite can be moulded into any form; all the little fancy articles made from bakelite are moulded when it is in this state. The moulded articles are baked; as the baking proceeds the bakelite becomes harder and harder.

The hardness of bakelite is due to its chemical structure. A molecule of formaldehyde is able to link up with two or more molecules of phenol; then other molecules of formaldehyde link up with the same phenol molecules. As the heating proceeds, the linkages spread in all directions; the longer the heating is continued the more complete is the system of links. The final product is neither soluble nor fusible. It

has the characteristics of a giant molecule, though the linkages are erratically arranged.

Among inorganic compounds the silicates are particularly prone to form giant molecules. Waterglass is sodium silicate. A solution of waterglass in water is often put on the surface of concrete ponds, to make them watertight ; it is put on with a paint-brush. The waterglass is absorbed by the slightly porous cement surface and forms a watertight layer over it. This layer is probably of the nature of a giant molecule, the silicon and oxygen forming a network of covalently linked atoms between the molecules of the cement.

Giant molecules still appear to be rather exceptional structures, but they are of more frequent occurrence than was formerly supposed. Regular three-dimensional giant molecules like the diamond are formed by such substances as carborundum, CSi , aluminium nitride, AlN , and beryllium oxide, BeO . Most resinous substances are now believed to form irregular giant molecules like bakelite. And several "layer-lattice" compounds, having a structure like that of graphite, are known ; mica, with its familiar "platey-ness," has a structure of this kind.

FIBRES.—There are also one-dimensional giant molecules, substances consisting of very long, thin molecules. Such substances are often fibrous in character.

We depend on fibres to quite an astonishing degree for the comfort of life. We are cushioned from blows by fibres and protected from the extremes of heat and cold by fibres. Our hair consists of fibres, the materials of our clothes consist of fibres, the structure of trees and plants depends on fibres, and the asbestos of our safety curtains is composed of fibres. In addition, many other important materials, such as rubber and paper, although not fibrous themselves, contain molecules of the same kind as those in materials which are fibrous.

The structure of fibres has been revealed by X-ray investigations, which are dealt with in a later chapter. Fibres consist of long, thin, submicroscopic crystallites or micelles : these crystallites are simply little bundles of the

long, thin molecules composing the fibre. Fibres are long and thin because the crystallites out of which they are built up are long and thin. The bundles of molecules usually lie lengthways, parallel to the long axis of the fibre; this is the case with silk, hair, and wool. Sometimes they are slightly inclined to the axis of the fibre; this is the case with cotton.

This kind of structure for fibres was originally suggested in order to explain their behaviour on wetting. When fibres absorb water they swell laterally much more than they swell longitudinally, perhaps fifteen times as much. If the fibres are twisted up spirally, as in a rope, the lateral swelling may even cause a decrease in length; it is well known that ropes shrink when they are wetted. The sideways swelling of the fibres makes the rope try to untwist. If the ends of the rope are fixed, it cannot do this; so the effect of

wetting the rope is just like twisting it up—it shortens the rope.

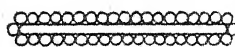


FIG. 13.—A crystallite covered with a layer of "adsorbed" water molecules.

It is easy to explain why fibres expand so much more laterally than lengthways on wetting. The adsorbed water covers the surface of the little crystallites, so that there is a layer

of uniform thickness over the surface of every crystallite. It is easily seen that the proportional expansion of the crystallite is very much greater laterally than longitudinally; and as the crystallites all lie in the same direction, the actual lateral swelling is much greater than the longitudinal.

Perhaps the most interesting thing about fibres is their elastic properties. The simplest case is found in silk fibres, for it is practically impossible to stretch the crystallites themselves at all. The crystallites of silk are already in fair alignment, and the first thing that happens on stretching a silk fibre is that they are drawn into still closer alignment. Very soon, however, the crystallites begin to slip past one another and take up new positions. When the tension in the fibre is released, the crystallites remain in their new positions, so that the fibre does not recover from this stretching. Silk fibres, in fact, show practically no true

elasticity; for true elasticity implies that the material returns to its original length after stretching.

This interpretation of the behaviour of silk fibres on stretching is confirmed by X-ray methods. By these methods we obtain photographs, "X-ray fibre photographs," each one characteristic of a particular fibre structure. It is found that the X-ray photographs of silk fibres show no essential change during the stretching of the silk. This is as we should expect, for the only change in the structure of the fibres is a slight increase in alignment of the crystallites.

The behaviour of animal hairs, "keratin," is quite different. When keratin fibres are sufficiently stretched, the X-ray photograph changes to an entirely different photograph; the original photograph returns when the fibres are allowed to contract again. Evidently we are dealing with a case of reversible intramolecular transformation; we have one kind of molecule in the unstretched fibre and another kind in the stretched fibre. The two forms are known as α -keratin, the unstretched form, and β -keratin, the stretched form.

What happens during the stretching of keratin is that the molecules uncoil. In α -keratin the molecules are bent round into what is very nearly a series of rings, while β -keratin contains an ordinary zigzag molecular chain. During the unwinding of these rings, the length of the molecule just about doubles itself, so that keratin fibres are capable of a 100 per cent. extension. They can recover completely from such an extension because the molecules simply coil themselves up again.

The behaviour of rubber is like that of keratin, except that in the unstretched condition rubber is not fibrous at all. The molecules in rubber are coiled up and arranged haphazard, whereas even in unstretched keratin the molecules are aligned parallel to one another and grouped into little

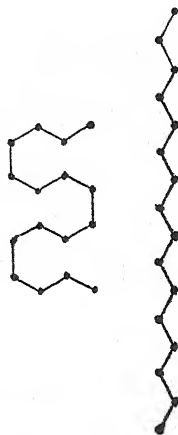


FIG. 14.—How the keratin molecule unwinds, and doubles its length, on stretching.

bundles (crystallites). When rubber is stretched, the molecules uncoil and align themselves, giving a structure like that of stretched keratin. This is why rubber can be stretched to such a remarkable extent—to ten times its original length—and yet recover more or less completely when it contracts again.

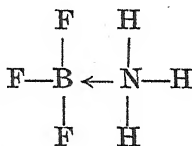
The difference between the two forms of keratin is utilised in the production of permanent waves in hair. In the extended form, the molecules of keratin are open to attack by steam, whereas the coiled-up form is unaffected. The water molecules in the steam attach themselves to the stretched keratin molecules and prevent them winding up again. Thus, if the hair is stretched and held in any desired position, it will be "set" in that position when it is steamed.

CHAPTER VIII

MORE ABOUT CHEMICAL LINKS

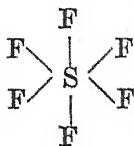
DONOR AND ACCEPTOR MOLECULES.—Very many compounds contain atoms with pairs of unshared electrons, and there seem to be ample opportunities for the formation of co-ordinate links. Besides other conditions, however, there are two very obvious ones which must be satisfied before a co-ordinate link can be formed. The first of these conditions is that there must be a molecule capable of donating one of its lone pairs toward a co-ordinate link : there must be a "donor" molecule. The second condition is that there must be a molecule capable of accepting the lone pair : there must be an "acceptor" molecule. These properties of donating and accepting lone pairs are associated with particular atoms in the molecules rather than with the molecule as a whole.

The case of ammonia has already been mentioned. Each of its atoms has an inert gas structure ; ammonia is, therefore, apparently a saturated compound. Nevertheless it readily forms co-ordinate links with other compounds. The reason is that the nitrogen atom has a lone pair of electrons, and nitrogen is a strong donor. The boron atom in boron trifluoride is a strong acceptor ; it has six electrons, all shared with the fluorine atoms ; it is, therefore, two electrons short of the octet, and it is ready to accept them from a suitable donor. With these two compounds, therefore, we have the conditions in which a co-ordinate link is formed. The compound resulting from their reaction is represented by :



The arrow, as usual, indicates the co-ordinate link and shows that the nitrogen atom is the donor and the boron atom the acceptor.

COVALENCY MAXIMA.—The outermost group of electrons in an atom is sometimes called the valency group. The commonest structure for a combined atom is that of one of the inert gases—with eight electrons in the outermost, valency, group (or two in the case of hydrogen). But these structures are far from being invariable ; there are numerous compounds in which one or other of the atoms has a valency group of more than eight. Sulphur hexafluoride, SF_6 , is one of these compounds. It is a very stable gas : it does not react with sodium, for example, below a red heat. Now a fluorine atom, having seven electrons in its outermost shell, can form one link only—with another fluorine atom, or with an atom of another element ; hence two fluorine atoms are never connected together except when fluorine occurs as an uncombined element. It is clear, then, that the fluorine atoms must each be united to the sulphur atom. The stability of the compound suggests that the links are ordinary covalent links. This would give the structure :



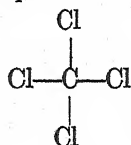
As each of the links represents two electrons, the sulphur atom in this compound has a valency group of twelve electrons. Its configuration is (2) (8) (12). The 12 is underlined to show that the electrons of the valency group are all shared, in this case with the fluorine atoms. (The structure is sometimes written : (2) (8) (6, 6).)

There are those who dispute this configuration and who hold that the outermost shell never has more than eight electrons. Those who hold this theory regard the links in SF_6 as consisting of two links each of two electrons, and four links of one electron each. On the view adopted here, that links of one electron are exceptional and usually unstable,

the stability of sulphur hexafluoride is conclusive evidence against the existence of such links in this compound.

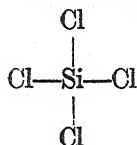
There is a definite limit to the covalency of any element—each element has a covalency maximum. Hydrogen can have a maximum valency group of two electrons: a covalency maximum of one. According to one theory, it may sometimes have a covalency of two; but this cannot be regarded as *conclusively* established, and the evidence of wave mechanics, for what it is worth, is against it. None of the elements of the first short period, lithium to fluorine, ever has more than eight electrons in the valency group; the covalency maximum is, therefore, four. In the second short period, sodium to chlorine, there may be as many as twelve electrons in the valency group; the covalency maximum is six. This is the period to which sulphur belongs. From rubidium onward there may be as many as sixteen electrons, with a covalency maximum of eight; and there are faint indications of as many as twenty toward the end of the table, from caesium onwards.

Carbon belongs to the first short period of elements, in which the valency group does not go beyond eight electrons. Carbon tetrachloride, CCl_4 , has the structure:



The carbon atom has its complete octet. It is not, therefore, an acceptor, because it cannot go beyond the eight. The lone pairs of the chlorine atoms are also unreactive, because chlorine is always a very weak donor. Hence this compound only reacts very sluggishly.

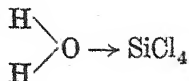
When we compare carbon tetrachloride with silicon tetrachloride, SiCl_4 , there is an obvious similarity in structure. The structure of silicon tetrachloride is:



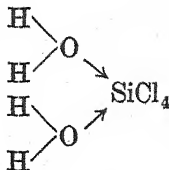
We might expect a corresponding similarity in properties. There are, however, several noteworthy differences in properties. Both carbon tetrachloride and silicon tetrachloride are colourless, volatile liquids; but the latter fumes when it is exposed to the air, while the former does not. This is because silicon tetrachloride reacts with the water vapour present in the air, whereas carbon tetrachloride does not react.

The difference arises from the fact that silicon belongs to the sodium-chlorine period, elements which can form valency groups up to twelve electrons. In silicon tetrachloride, the silicon atom has a valency group of eight; so it can act as an acceptor and increase its valency group to ten or twelve. This is, of course, impossible for carbon in carbon tetrachloride.

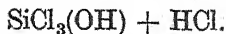
Water is a donor molecule, so it reacts with silicon tetrachloride to give first :



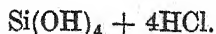
One of the lone pairs of the oxygen atom co-ordinates on to the silicon, increasing the valency group of the silicon from eight to ten. Two water molecules may co-ordinate on in this way, giving :



Let us suppose that only one water molecule co-ordinates on. The next thing that happens is that a molecule of HCl is lost, giving

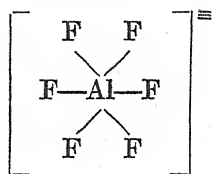


The net result is a replacement of a chlorine atom by a hydroxyl, OH, group. Repetition of the process gives eventually :



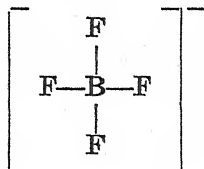
The mineral cryolite, which has the formula $\text{Na}_3[\text{AlF}_6]$ is interesting because of its low melting-point. It was originally discovered in South Greenland. The name "cryolite" means "ice-stone"; the mineral was given this name by the Eskimos, who imagined it to be a kind of specially frozen ice—it will actually melt in a candle flame.

The aluminium atom in the $\text{AlF}_6^{=}$ ion of cryolite has a valency group of twelve electrons—two from each of the six links with the fluorine atoms :



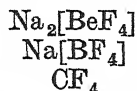
The three positive charges on the three sodium ions of cryolite balance the three negative charges on the $\text{AlF}_6^{=}$ ion.

Aluminium falls in the sodium-chlorine period, so there is nothing surprising about its having a valency group of twelve. If we consider boron, the corresponding element in the lithium-fluorine period, its valency group can only reach eight electrons. So there is no compound $\text{Na}_3[\text{BF}_6]$, but only $\text{Na}[\text{BF}_4]$. In the BF_4^{-} ion



the boron forms four covalencies, the maximum possible in this period. The negative charge on the ion is balanced by the positive charge on the sodium atom in $\text{Na}[\text{BF}_4]$.

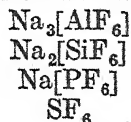
These two compounds, $\text{Na}_3[\text{AlF}_6]$ and $\text{Na}[\text{BF}_4]$ each fall in a series. In the first short period we have the series :



Each of the elements beryllium, boron, and carbon can form

not more than four covalencies, so they can only link up with four fluorine atoms. The negative charge on the $[XF_4]$ ($X = \text{Be, B, or C}$) decreases one by one as we go down the series. The BeF_4^- ion has two negative charges, the BF_4^- ion has one negative charge, and CF_4 has zero charge. This is because the positive charge on the nucleus increases one by one from beryllium to boron and then to carbon.

In the second short period we have the series :



$\text{Na}[\text{PF}_6]$ was discovered quite recently and completes this interesting series. Here the covalency maximum is six, each atom—aluminium, silicon, phosphorus, or sulphur—can form co-ordinate links with six fluorine atoms. As before, the negative charge on the complex decreases one by one down the series.

These two series bring out very clearly the covalency maximum of four in the lithium-fluorine period and of six in the sodium-chlorine period.

THE TRANSITION ELEMENTS.—The transition elements are characterised by the fact that the electrons in the outermost shell can go into the shell immediately below. This facility for interchange of electrons between the two outer shells enables the transition elements to form a great variety of compounds. They have very varying valencies. Titanium, for instance, can have any of the valencies 2, 3 or 4; manganese can have any of the valencies 1, 2, 3, 4, 6, or 7; and so on through all the transition elements.

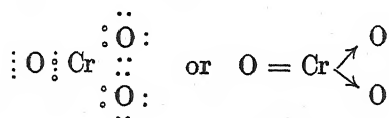
The particular case of chromium illustrates how the electrons change over from shell to shell, and how this leads to a multiplicity of valencies.

In the metallic state chromium has the structure (2) (8) (13) (1). As usual the outermost electron can readily be lost. The loss of this electron gives the atom the structure (2) (8) (13), leaving it with a net positive charge of one. This structure is not stable because of the large number of

electrons in what is now the outermost shell; another electron is lost, giving the structure (2) (8) (12) with a net positive charge of two. This is the chromous ion, Cr^{++} . Even the structure of the chromous ion is not very stable; chemical action readily removes another electron and the structure becomes (2) (8) (11) with three net positive charges; this is the chromic ion, Cr^{+++} . This is stable because the chromium nucleus, with 24 positive charges, can hold 11 electrons in the third shell, although it can barely hold 12 and cannot hold 13 without any stabilising electrons in the fourth group.

In forming the chromous ion, Cr^{++} , one electron is removed from the outermost shell and one from the shell below; in the case of the chromic ion one electron is removed from the outermost shell and two from the shell below. These ions give rise to two series of ionised compounds: chromous compounds containing the divalent chromous ion, and chromic compounds containing the trivalent chromic ion.

Chromium can also form covalent compounds, such as the trioxide, CrO_3 . This has the structure:



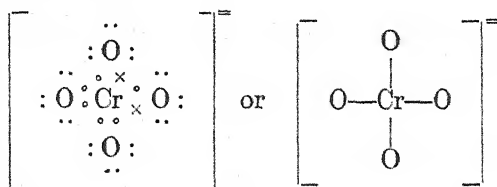
(The double line represents two covalent links, each consisting of two electrons, one supplied by the oxygen atom and one by the chromium atom in each link. The arrows represent co-ordinate links, each of two electrons, and all supplied by the chromium atom.)

Altogether the chromium atom supplies six electrons toward the links, of which five come from the third shell. Chromium here has a valency of six in the old sense of the word, or, as we should now say, four covalencies. The six electrons supplied by the chromium atom are all it has in excess of the stable argon structure (2) (8) (8). The configuration of the electrons in the chromium atom in this compound is written: (2) (8) (8) (8). The underlined 8 represents the eight electrons in the links, six from the

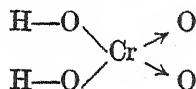
chromium and two from one of the oxygen atoms; the underline shows that the electrons are all shared. Sometimes the shared electrons are written as two equal groups: in this case as (2) (8) (8) (4, 4).

We can write the structures of the oxygen atoms in a similar way. The structure of the atom held by a double link is: (2) (4, 4); there are eight electrons in the outer group; four are unshared and four (underlined) are shared. The structure of each atom held by a co-ordinate link is written: (2) (6, 2); only two of the electrons are shared.

Chromium also forms the ion $\text{CrO}_4^{=}$; this is the chromate ion. Its structure is:



It corresponds to chromic acid, which has the structure



The structure of the chromium atom in the chromate ion is (2) (8) (8) (8); that of each oxygen atom is (2) (6, 2). Here again the chromium atom has six valencies—the four covalencies and the two electrovalencies indicated by the minus signs.

There is a close relationship between the chromate ion and chromium trioxide. In each case the chromium atom has four covalencies, and in each it is hexavalent in the old sense. They are closely related chemically as well as structurally. When chromium trioxide dissolves in water it gives chromic acid, the acid from which the chromates are derived.

In this transition element, chromium, we have seen a great variety in the number of electrons in the outer shell, and the corresponding variety of valency in forming com-

pounds; we have seen that the outer electrons may be stripped away and that electrons of the shell below may then assist in valency formation. This behaviour is regarded as abnormal; it only occurs with transition elements and to a lesser extent with a few elements close to them in the periodic table. Normally the task of valency formation is left entirely to the outermost shell of electrons.

The transition elements come nearest to the normal behaviour in their highest valency state, when there is a complete outer octet of electrons. In the chromate ion, $\text{CrO}_4^{=}$, the chromium atom has the configuration (2) (8) (8) (8). Since the outer electrons are all shared with the oxygen atoms, there is no tendency for any of them to go into the third shell; that is why the chromate ion approaches the normal behaviour.

The structure of the chromate ion is very similar to that of the quite normal sulphate ion, $\text{SO}_4^{=}$. The structure of the sulphur atom in the sulphate ion is (2) (8) (8). (Compare this with the structure of the chromium atom in the chromate ion—(2) (8) (8) (8).) The similarity of structure between the two ions, $\text{CrO}_4^{=}$ and $\text{SO}_4^{=}$, is shown in the fact that chromates and sulphates often have the same crystalline forms (they are isomorphous).

Manganese is another example of a transition element which approaches normal behaviour in its highest valency state. In the permanganate ion, MnO_4^{-} , the manganese atom has the structure (2) (8) (8) (8). This structure closely resembles that of the chlorine atom in the perchlorate ion, ClO_4^{-} ; the behaviour of chlorine is regarded as normal; the chlorine atom in the perchlorate ion has the structure (2) (8) (8). Here again we find similarity of behaviour going along with similarity of structure. Almost the only resemblance between manganese and chlorine is in the behaviour of these ions: for example, the potassium salts, KMnO_4 and KClO_4 , are isomorphous.

In addition to the variety of valencies and the corresponding variety of compounds, the transition elements are also characterised by the bright and varied colours of their

compounds. In the chromic ion, Cr^{+++} , the configuration is (2) (8) (11) with a net positive charge of three. There is room for eighteen orbits in the third shell, and only eleven of the orbits are occupied. The eleven electrons can jump from orbit to orbit in a way that would be impossible if all the orbits were already filled. When electrons make such jumps they absorb visible light of definite colour, so that the chromic ion, and all similar ions, appear coloured. The colour of the chromic ion is dark green.

The change from the waywardness and many-sidedness of the transition elements comes rather gradually. The element following them in the periodic table is copper, (2) (8) (18) (1), with its third shell of electrons complete. The return to the normal, to sobriety, is beginning. But copper is not quite normal; the glory is not quite departed. Copper can lose its outermost electron and become the cuprous ion, Cu^+ , with the structure (2) (8) (18) with a net charge of plus one. The cuprous ion is not stable under all conditions; the positive charge on the nucleus cannot always restrain the mutual repulsions of the whole eighteen electrons. One of the electrons is readily driven out; this changes the cuprous ion into the cupric ion, Cu^{++} , with the structure (2) (8) (17) with a net charge of plus two. Corresponding to the ions there are series of cuprous and cupric compounds.

Zinc, the element following copper, has the structure (2) (8) (18) (2). When it loses its outer electrons it becomes the zinc ion, Zn^{++} with the structure (2) (8) (18) with a net charge of plus two. The positive charge on the nucleus is, of course, one unit higher than the charge on the copper nucleus. This enables the nucleus to hold the large group of eighteen electrons in place, in all but the most exceptional conditions.

Beyond zinc, none of the other elements of the first long period shows any tendency for the electrons in the third shells to become involved in valency formation. That task is left entirely to the electrons of the outermost shell, the normal state of affairs.

COVALENT AND ELECTROVALENT COMPOUNDS.—It is useful

to be able to distinguish between compounds formed by covalency and those formed by electrovalency.

The simplest method is to try to dissolve the substance being tested, in various liquids. Now there are two groups of solvents of which water and benzene are extreme examples. Water usually ionises substances dissolved in it, although not by any means always. Benzene is always a non-ionising solvent. If a substance dissolves in benzene, this is almost certain proof that it is a covalent compound. If a substance dissolves in water, it is more probable than not that it is electrovalent; but there is no certainty. A conclusive test is to find whether the solution will conduct electricity. The current is carried by ions—positive ions in one direction, negative in the other—so that only solutions of ionised substances will conduct electricity. (An "ionised" compound is the same thing as an "electrovalent" compound.)

There is, however, no rigid classification of substances into covalent and electrovalent compounds. Some substances may be the one or the other according to the liquid in which they are dissolved. Hydrogen chloride, HCl , may be either the covalent compound $\text{H}-\text{Cl}$, or the ionised compound $\text{H}[\text{Cl}]$; the transition from one form to the other is easily made. When it is dissolved in water, hydrogen chloride is ionised, and therefore the solution conducts electricity. When it is dissolved in benzene it is not ionised and the solution does not conduct electricity. Again, even in ionising solvents, compounds are very often not completely ionised: some of their molecules are ionised whilst some are covalently linked together.

The boiling point is another indication as to whether a compound is electrovalent or covalent. In covalent compounds electrostatic attraction is comparatively unimportant; the external electric field of a molecule hardly extends beyond the molecule itself. Consequently there is little electrostatic attraction between the molecules, they are but weakly held together, and they are readily separated. Now vaporization involves a certain separation of the molecules; so covalent molecules are easily vaporized,

the compound has a low boiling point. In electrovalent (ionised) compounds each ion has its own charge, and there is great electrostatic attraction between the ions; for this reason they are difficult to separate. Hence it occurs that in electrovalent compounds it is comparatively difficult to separate the molecules so as to vaporize the compound; electrovalent compounds have, therefore, comparatively high boiling points.

Sodium chloride, NaCl , has a boiling point of $1,441^{\circ}\text{C}.$; oxygen, O_2 , has a boiling point of $-183^{\circ}\text{C}.$ These boiling points are clear indications that common salt is ionised and that oxygen is un-ionised. This is confirmed from other sources.

But there are other things which affect the boiling point, in addition to the nature of the links; chief amongst these are the size and weight of the molecules. Heavy molecules are less easy to stir into the activity of the vaporized state, and therefore substances whose molecules are heavy tend to have higher boiling points than substances with lighter molecules.

Aluminium trichloride, AlCl_3 or rather $(\text{AlCl}_3)_2$, has a boiling point of $183^{\circ}\text{C}.$, and this rather high boiling point might be taken as an indication that it is an electrovalent compound. But when we compare this substance with, say, oxygen, we find that the molecules are much heavier. It has a molecular weight of 133, compared with oxygen's 32. In addition to this the molecules are probably polymerised—they exist as double molecules—and therefore we have to double the 133. With such heavy molecules $183^{\circ}\text{C}.$ is within the temperature region which indicates that compounds are un-ionised.

An examination of the space-arrangement of the atoms in a molecule (by the methods of stereochemistry in general, and by the study of crystal structure in particular) is still another method of deciding whether a compound is electrovalent or not. In ionised compounds the electrovalencies have no particular directions in space. In covalent compounds the atoms have definite positions in space relative to one another. The atoms may, for instance, have a linear

arrangement, as in carbon dioxide, or they may be arranged at the centre and corners of a tetrahedron, an arrangement which is found in most carbon compounds.

There is a special method which is sometimes available for the detection of small traces of ionisation. It can be applied, for instance, to lead compounds. Thorium B is a radioactive element, and it is an isotope of lead ; it has all the chemical properties of lead. It is, in addition, by virtue of its radioactive properties, capable of detection and measurement even when present in minute quantities. If, now, we take lead chloride and lead nitrate, we can introduce a little thorium B into one of the compounds. If we mix together the lead chloride and the lead nitrate, the thorium B distributes itself proportionately between the two compounds ; if we separate out the two compounds again, each contains the same proportion of thorium B. This is because the two compounds are ionised ; when they are mixed there is a continual interchange of lead atoms between them.

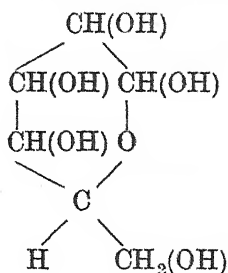
If, however, we take lead nitrate and lead tetraphenyl, $\text{Pb}(\text{C}_6\text{H}_5)_4$, there is no such interchange of lead atoms because the lead tetraphenyl is not ionised at all. The thorium B all remains in the compound in which it was first introduced.

With lead tetra-acetate, $\text{Pb}(\text{O}.\text{CO}.\text{CH}_3)_4$, and lead nitrate there is an interchange of lead atoms. Thus lead tetra-acetate must be feebly ionised ; yet the ionisation is too feeble to be detected by any other method.

This principle of this method is, as it were, to label some of the lead atoms (by making use of the radioactivity of thorium B) and then see what happens to them. The same principle has been applied to hydrogen ; heavy hydrogen is used to "label" some of the atoms—we can follow what happens to the heavy atoms in a mixture. It has been found, for example, that when heavy hydrogen is confined over ordinary water, the heavy hydrogen distributes itself between the gas and the water ; just as thorium B distributes itself between lead chloride and lead nitrate. This distribution of heavy hydrogen is greatly accelerated in the presence of platinum. It is, indeed, probable that the distribution

cannot take place at ordinary temperatures except in the presence of some such substance as platinum ; in silica vessels no distribution occurs at all. In the original experiments it is likely that the glass of the vessels used was able to bring about the reaction.

When the method is applied to a sugar of the formula :



it is found that five of the hydrogen atoms in the sugar are capable of interchange but seven are not. It is probable that the five hydrogen atoms in the five OH groups are capable of ionisation, and hence can interchange ; whereas the seven hydrogen atoms attached to the carbon atoms are unable to ionise.

CHAPTER IX

WAVE MECHANICS AND THE CHEMICAL LINK

BOHR's theory of the atom explains a great deal about the structure of atoms and molecules, but it does not offer a complete explanation or anything like a complete explanation. It leaves a vagueness about the chemical link, for example. We know that the chemical link is formed by two electrons and that these two electrons are shared by the linked atoms. So far so good. But "shared" is a vague word; it offers a partial solution of one problem, and at once raises another—in what sense are the electrons shared by the linked atoms?

One rather obvious suggestion was that the electrons forming the link circulate round the nuclei of both atoms and thus hold the two together—like an indiarubber band. Unfortunately this simple idea raises great mathematical difficulties and it has to be discarded as useless. Then the suggestion was made that the electrons travel in a figure-of-eight orbit, with one nucleus in each loop of the eight. This idea also had to be given up because it led nowhere. It is probable that the electrons *do* circulate round both nuclei, but it is useless to approach the problem by considering the actual orbit in which they travel.

The Bohr theory is inadequate in other directions too. It leaves out of account, for example, all questions as to the structure of the nucleus. It does give considerable help in the study of spectral lines; it enables the positions of some lines to be calculated, but it is of no use in finding their intensities. Moreover, spectroscopists have discovered a number of useful empirical rules and formulæ which hold quite accurately. Bohr's theory gave hints as to the sort of formulæ to look for; but the deductions from this theory differed in small but significant details from the results

discovered empirically. [For instance, it was deduced from the old quantum theory, that the energy of a linear oscillator should have the values : 1 quantum, 2 quanta, 3 quanta, etc. ; whereas the spectroscopic results were better accounted for by supposing that the possible values are : $\frac{1}{2}$ quantum, $1\frac{1}{2}$ quanta, $2\frac{1}{2}$ quanta, etc.]

Altogether there are too many buts about Bohr's theory. A new method of approach to atomic problems is needed. This new method of approach has been supplied by Schrödinger and other workers in atomic physics, who gave up the Bohr idea altogether. Schrödinger, by a series of inspired leaps in the dark—one can scarcely analyse the process any farther than that : it was inspiration—obtained the "wave equation" which forms the basis of wave mechanics.

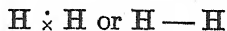
There is no general agreement as to the precise physical significance of the wave equation. But we do know that it works : it gives results in agreement with the observed phenomena, and enables us to make predictions about new phenomena.

It is hardly to be expected that an equation of such a fundamental nature should be easy to manipulate. If we try and apply it to a complicated system we shall probably find that the equation takes on a form too difficult to solve. Even in quite simple systems we often have to make drastic approximations (which sometimes amount almost to guessing the answer) before the equation can be solved.

The wave equation has been applied to a great variety of atomic problems. If it is applied to an electron bound to a positive nucleus—to the hydrogen atom, for example—we can deduce that there are four quantum numbers associated with the electron and that these numbers have the properties we have already ascribed to the principal, azimuthal, magnetic, and spin quantum numbers. We can apply the wave equation to the problem of electronic transitions between different energy levels in the atom ; we can calculate the relative probability of these transitions, and hence the relative intensities of the lines to which they correspond in the spectrum. The fundamental nature of the wave

equation can be realised when it is pointed out that it has been applied to such varied phenomena as : the speed of reactions, the structure of the nucleus and the disintegration of the radioactive elements, the problem of the chemical link and its direction in space, the scattering of X-rays and electrons by atoms, the conductivity of electrolytes and the phenomenon of overvoltage, the quenching of fluorescence by traces of impurities, and so on.

At the moment we are concerned with the application of the wave equation to the problem of the chemical link. The simplest case of chemical combination is the union of two neutral hydrogen atoms to form a hydrogen molecule :



The wave equation enables us to calculate the potential energy of this system of two hydrogen atoms for various interatomic distances—the interatomic distance refers to the distance between the two hydrogen nuclei. (Kinetic energy is energy of motion, the kind of energy possessed by a moving body. Potential energy is not immediately apparent as movement. A wound-up clock-spring, for example, is a reservoir of potential energy ; but there is no sign of its existence until the spring is permitted to unwind.)

Heitler and London made this calculation of the potential energy of a system of two neutral hydrogen atoms. The wave equation yielded two solutions ; APQ and BRST are the graphs of these solutions. Thus, on the curve APQ, PL represents the potential energy of the system when the atoms are at a distance OL apart.

It will be remembered that an electron revolving in its orbit in a hydrogen atom is spinning one way or the other. If we consider a pair of hydrogen atoms, there are two possibilities : either their electrons have spins in the same direction [both have $s = +\frac{1}{2}$ or both have $s = -\frac{1}{2}$], or else the spins are in opposite directions [one has $s = +\frac{1}{2}$ and the other has $s = -\frac{1}{2}$]. These two possibilities correspond to the two solutions found by Heitler and London.

When the spins of the electrons are in the same direction we get the curve APQ ; this is called the symmetrical case,

As the atoms move farther apart, say from a distance OL apart to a distance OM apart, the potential energy decreases from PL to QM; some of the potential energy has changed into kinetic energy, energy of motion. Now potential energy always changes into kinetic energy when it can; a wound-up clock-spring begins to unwind as soon as it is released. So, since it involves the conversion of potential into kinetic energy, the two hydrogen atoms tend to move farther apart; they move faster and faster away from each other because more and more potential energy is being converted into kinetic energy. The atoms are repelling one

another, and there is obviously nothing in the nature of a chemical link; there is no possibility of chemical combination.

When the electrons of the two hydrogen atoms spin in opposite directions we have the antisymmetrical case; the potential energy of this system is plotted in the curve BRST. There is an obvious and important difference

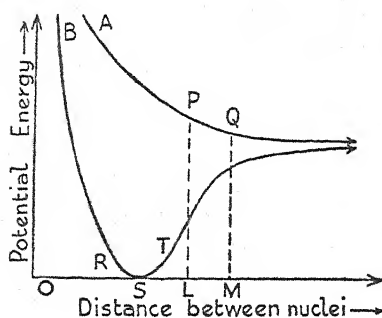


FIG. 15.—The two solutions of the wave equation for the hydrogen molecule.

between this case and the symmetrical case: the upper curve falls steadily from A onward, showing a continuous decrease in the potential energy as the atoms get farther apart; the lower curve falls as far as S and then rises again. The point S is a minimum of potential energy. If the atoms move from R toward S, or from T toward S, in both cases their potential energy is decreasing. Since potential energy always decreases when it can, the atoms will always tend to come to a distance OS apart, whether they are closer in or farther out than OS. Thus the distance OS corresponds to a state of equilibrium; if the atoms are slightly disturbed, they tend to return to this distance apart.

This, then, is the case which corresponds to chemical com-

bination. In a molecule of hydrogen the atoms, we know, are fixed at a certain distance apart, and we have just seen that in the antisymmetrical case the atoms *are* fixed like this. The chemical link thus appears as two electrons of opposite spin ; the spins are, so to speak, paired off in the process.

It is the minimum in the potential-energy curve for the antisymmetrical case that leads to the chemical combination in that case. But why do we get a minimum in the curve at all ? The potential energy is made up in two ways. First of all there is the energy due to the attractions and repulsions of the charged particles in the molecule—the electrostatic energy. There is no difficulty about this : its existence has been recognised ever since the structure of the atom was elucidated. There is also another kind of energy, whose existence was unknown until the advent of wave mechanics, called exchange energy or resonance energy. When two hydrogen atoms approach one another, a kind of resonance effect occurs. There is an energy, the exchange energy, associated with this process of resonance ; the net result may be either an increase or a decrease in the total energy of the system, according as the spins of the electrons are in the same or in opposite directions. The minimum in the potential-energy curve for the hydrogen molecule is due to this decrease in the total energy when the spins of the electrons are opposed.

When once the link between two hydrogen atoms has been set up, a remarkable thing occurs. The quantum-mechanical resonance—as it is called—between the atoms, leads to a very rapid backwards and forwards flow of the energy of the link. This phenomenon helps to explain both the strength of the link and the unity of the linked atoms.

An attempt has been made, with some success, to generalise these results on the hydrogen molecule into a universal theory of covalency. A few other cases have been investigated with something of the same degree of approximation as the hydrogen case. For instance, it has been shown that a hydrogen atom and a helium atom repel one another at all

distances ; there is no position of equilibrium where the atoms remain more or less fixed in place, so there is no chemical combination. This agrees, of course, with the observed facts. Another case is that of two helium atoms. Here there is repulsion ; but at comparatively large distances there is a weak attraction. [The minimum in the potential-energy curve is very shallow.] This weak attraction, the "van der Waals attraction," hardly affects the question ; for collisions with other atoms soon break up any "van der Waals molecules" held together by this attraction. Nevertheless it is the van der Waals attraction that

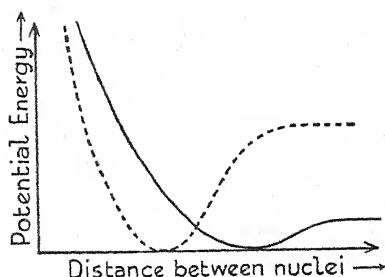


FIG. 16.—The potential-energy curve of a van der Waals molecule. The dotted curve is the potential-energy curve of an ordinary molecule. The minimum in the van der Waals curve is much shallower and farther out.

causes gases to liquefy, and molecules held together by this force are of some importance in the study of molecular spectra.

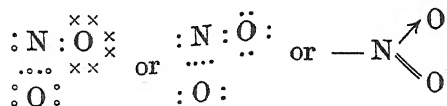
Not all molecules can be investigated by the methods of wave mechanics with the same degree of exactness as is possible in the case of the hydrogen molecule. In other cases we must use more approximate methods. One way is

to argue from the analogy of the hydrogen case, that covalencies in general consist of pairs of electrons of opposite spin. This procedure has had considerable success in predicting the stability of compounds, the directions of covalent links in space, and so on.

In this theory of covalency, the idea of quantum-mechanical resonance plays a considerable part ; although, like most new ideas, it has been rather overworked. It is the existence of this phenomenon that makes the formation of molecules possible at all. In general, resonance occurs whenever a molecule can exist in two states with the same or very nearly the same amount of energy ; we say that there

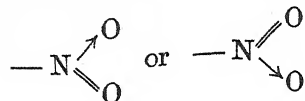
is quantum-mechanical resonance between the two states. The molecule is neither in one state nor the other, but in an intermediate state of very rapid transition from one to the other.

This quantum-mechanical resonance probably accounts for the fact that some molecules behave as though they were more symmetrical than their formulæ would indicate. The nitro-group, for instance, has the formula :



(The nitro-group does not exist alone, but is always attached by a single link to some other group, such as the methyl group, CH_3 . The union of these two groups gives the compound, nitromethane, $\text{CH}_3\text{-NO}_2$.) The two oxygen atoms in nitromethane are linked in different ways to the nitrogen atom : one is attached by a co-ordinate link consisting of two electrons, and the other is attached by a double link consisting of four electrons. Yet there exists no difference between the two oxygen atoms which can be detected experimentally.

It is suggested that the two oxygen atoms in the nitro-group can change rôles, so that the group can be either :



The two forms are identical and have exactly the same energy content. This is the very condition for quantum-mechanical resonance. A particular oxygen atom is held neither by a co-ordinate nor by a double link, but by something intermediate between the two, such as would arise if there were a very rapid transition between the two structures just given.

Besides this theory, based primarily on the idea of the covalent link as a pair of electrons of opposite spin, there is another method of approach to the problem of the chemical

link. The procedure in this method is to start off by putting into place the positive nuclei of the atoms in the compound under consideration. Then the effect of introducing the electrons one by one is investigated. Of course, this method and the previous method of treatment of the problem of the covalent link should give just the same results; but in both methods it is necessary to carry out drastic approximations, so that the final results are often different. It is a matter of choosing which method is the easier to manipulate, and which introduces the more reasonable set of approximations.

The second method of approach, due to Hund, Mulliken, and others, gives up the idea that the electrons are localised in any particular chemical link. Each electron is supposed to perambulate all over the molecule, although it frequently happens that a particular pair of electrons spends perhaps 99 per cent. of its time in one particular link. The ordinary electron-pair bond of the Heitler-London theory is thus merely an extreme case, in which a pair of electrons is almost entirely in one particular link. There is a continuous gradation from this extreme case to the other extreme when the electrons spend hardly any of their time in the link, so that the link is very weak. In the latter extreme case a link has practically disappeared, so that a compound of abnormal valency—with one link fewer than usual—arises.

There is thus a sort of "smearing out" of valency in this theory. The theory has the merit of bringing a number of compounds of abnormal valency into line with normal compounds; normal compounds are regarded as extreme cases in which the electrons spend so much of their time in one particular link that they are to all intents and purposes localised there. On the other hand, compounds of normal valency exceed greatly in number those of abnormal valency; there is a danger in the Hund-Mulliken theory of over-emphasising the abnormal compounds. In smearing out the idea of valency we must take care we do not smear it away altogether.

THE TUNNEL EFFECT.—If you think of a carriage running on a switchback railway, when it is near the bottom of the

slope it is running very fast, and when it is near the top it is running slowly. At the bottom it has a lot of kinetic energy, but at the top it has only a little. This is because its kinetic energy changes to potential energy as it runs up to the top of the slope; it possesses this potential energy simply because of its position, because it is high up the slope.

The hill on a switchback railway is a potential-energy barrier. The carriage cannot get over the hill unless it has enough energy to reach the top of the hill. The energy of the carriage is kinetic at the bottom of the hill, and is converted into potential energy as it reaches the top; so that the sum of kinetic energy *plus* potential energy is always the same.

A potential-energy barrier need not necessarily be such a thing as a hill. Such barriers exist wherever a forward movement entails an increase in potential energy—as it did in the case of the upward slope of the hill.

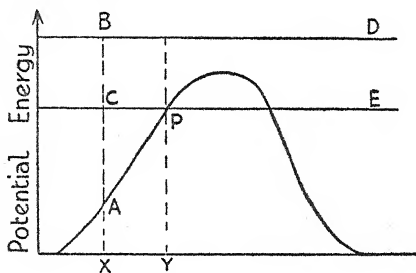


FIG. 17.—Potential-energy barrier.

For the carriage to get from one side of the hill to the other, it has to climb to the top of the hill; so it must have enough energy to carry it to the highest point on the hill. According to the classical theory of mechanics the same sort of thing is true of every potential-energy barrier: to pass the barrier, the particle in question must have sufficient energy to carry it to the top point on the potential-energy curve. Consider the particle at the point A on the potential-energy curve in Fig. 17. The particle has potential-energy equal to AX [actually, of course, the potential-energy involves an arbitrary additive constant], and it has kinetic energy equal to AB, say. Now its total energy is constant and represented by the line BD; this line lies above the barrier, so the particle is able to cross the barrier. If, however, the kinetic energy of the particle when it is at A is given by AC, then its total energy is represented by CE.

This line lies below the barrier, so in this case the particle is unable to cross the barrier. For suppose the particle reaches the point P. Here all its energy is potential energy (equal to PY) and none of the energy is kinetic. In other words, the particle is at rest; it cannot get any farther along the curve, it can only fall back on the side it started from.

Wave mechanics, however, gives a different answer. According to wave mechanics a particle can get across a barrier, even if its energy is not enough to carry it to the top of the barrier. Classical mechanics divides particles trying to cross the barrier into two classes: those that have sufficient energy to get across, and those that have not sufficient energy. Wave mechanics makes no such division; all particles possess a chance of getting from one side of the barrier to a position of equal energy on the other side. The larger the energy of the particle, the greater its chance of crossing the barrier; but it may get across even if its energy is insufficient to take it to the highest point on the barrier.

This may seem surprising. How can a carriage on a switchback railway get across a hill without going to the top of the hill? Of course, the carriage might be able to find an alternative path, easier than that across the hill; but that is irrelevant—no question of an alternative path arises in the effect we have just been considering.

The fact is that the ideas of energy and so on which are adequate to explain the behaviour of ordinary-sized objects—like the carriage on the switchback railway—are not adequate when we come to small particles like the electron. We want a new picture. According to wave mechanics, there are waves associated with moving particles, and these waves spread out in all directions. They spread out on both sides of an energy barrier. This creates a possibility of a particle on one side of the barrier finding itself on the other side. It is as though the particle had tunnelled through the barrier, and for this reason the effect is called the tunnel effect. The effect is known by other names, such as "quantum-mechanical leakage through a barrier."

Wave mechanics enables us to calculate the chance of a particle getting through a potential-energy barrier; or if

there are a lot of particles, the number passing through in unit time. Gamow applied the theory to the problem of the emission of alpha-particles by radioactive substances. The particles are emitted haphazard; but over a long enough time the rate of emission averages out into an even curve. Each radioactive element has its own "half-life period," that is, the time taken for half its atoms to disintegrate. In the case of radium, for example, the half-life period is 1,730 years. Half the total amount of radium disintegrates in this period, half of the remainder in the next 1,730 years, and so on. From the half-life period we can easily calculate the number of alpha-particles emitted by, say, a gram of radium in a second.

The half-life period of an element is related in a simple manner to the range of the emitted alpha-particles. [The relation is :

$$\log \lambda = A + B \log R$$

where λ is the half-life period, R is the range of the alpha-particles in air at N.T.P., and A and B are constants. This relation is called the Geiger-Nuttall relation.] To account for this relation had remained an unsolved problem, until the recent application of the tunnel effect to it.

There is a potential-energy barrier to the emission of alpha-particles; wave mechanics enables us to calculate how often an alpha-particle can get across this barrier. It also gives us the speed of the alpha-particles. The speed determines the range; the faster the particles travel, the farther they go before they are brought to rest, that is, the longer the range. We thus reach eventually a relation between the half-life period and the range; the relation is the same as the one discovered experimentally.

The tunnel effect has been applied also to explain the phenomenon of overvoltage. In electrolysis it is often observed that electrolysis does not actually begin as soon as we should expect. It is necessary to apply a distinctly larger voltage than we should expect before an appreciable amount of electrolysis will occur. It is this excess voltage which is known as overvoltage. The phenomenon has been explained by taking into account the potential-energy

barrier at the surface of an electrode in a solution; this barrier checks the passage of electrons between the electrode and the solution. The overvoltage potential is necessary to overcome the effect of this barrier and force an appreciable number of electrons through it.

The tunnel effect enables us to investigate quantitatively the passage of electrons through this barrier, and gives the first real explanation of overvoltage.

Another field where the tunnel effect has been applied is that of the speed of reactions. In this case the energy of activation, the amount of energy a molecule must have before it will react, forms a potential-energy barrier. This problem has been treated with great success by the classical theory; the introduction of wave mechanics, however, enables us to calculate the actual value of the energy of activation and also to recalculate the chance of a molecule getting through the barrier formed by this energy of activation. The latter effect comes out very much the same as that calculated from the classical theory; it is only when a hydrogen atom is involved in a reaction that the tunnel effect is of importance. As often happens with new ideas, the tunnel effect has been applied, often with more enthusiasm than discretion, to a great many problems. It must, of course, be applicable whenever the question of the leakage of particles through a barrier arises. But when the calculations are actually carried through, it is found in many cases that the tunnel effect has only introduced a small correction to the results obtained by the classical theory.

ORTHO- AND PARA-HYDROGEN.—We have already discussed the unexpected discovery of the heavy isotope of hydrogen. But that is not the only surprising thing that has been discovered about hydrogen in the last few years.

It was predicted from wave-mechanics that the molecules in hydrogen gas are not all alike, as was formerly supposed; instead there are two kinds of hydrogen molecule. The hydrogen molecule contains two nuclei (protons), and these nuclei are spinning. The spins may be in the same direction, in which case we have a molecule of "ortho-hydrogen"; or they may be in opposite directions, when we have a molecule

of "para-hydrogen." (These nuclear spins must not be confused with the spins of the electrons, which are involved in the formation of a covalent link.)

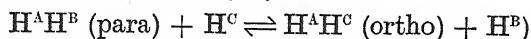
The two forms of hydrogen differ in their properties, although the differences are not so remarkable as those between hydrogen and heavy hydrogen.

Ordinary hydrogen consists of a mixture of about one part of para- to three parts of ortho-hydrogen. On cooling hydrogen to the temperature of liquid hydrogen the ortho-begins to change into the para-form ; if a little charcoal or platinum is present, this change takes place rapidly and eventually practically pure para-hydrogen is produced. If we now take away the charcoal or platinum and warm up the gas, we have a practically pure sample of para-hydrogen, and we can investigate its properties.

Ortho- and para-hydrogen differ slightly in such properties as specific heat, and they differ spectroscopically. The most interesting thing about them is, however, their conversion into one another. We have seen already that this change does not take place at ordinary temperatures unless a little charcoal or platinum is present. At high temperatures, the two forms can be converted into one another in the absence of such substances as charcoal ; the speed of the conversion indicates that the reaction is :



(The ordinary formulæ are a little inadequate here. Perhaps it is better to letter the three hydrogen atoms involved in the reaction A, B, and C :



One thing should be pointed out : an ordinary collision with another molecule seems incapable of changing the spin of one of the nuclei, and so changing ortho-into para-hydrogen or *vice versa*.

CHAPTER X

POLAR MOLECULES

EVERYONE knows about the two equal poles of a magnet, the north pole near one end and the south pole near the other; the magnet can be described as a dipole. There is another kind of dipole which consists of a positive and an equal negative electric charge some distance apart. Molecules are often minute dipoles. If you think of all the negative charges in a molecule, there is a single negative charge, acting at a definite point, that would have the same effect as all the negative charges put together; that single charge is the resultant of all the negative charges. (Just as the weights of all the separate particles of a body sum up to the whole weight pulling at the centre of gravity.) The positive charges also have a positive resultant acting at a definite point.

The molecule as a whole is electrically neutral, so the resultant of all the negative charges must be equal to the resultant of all the positive charges.

It may happen that the two resultants act at the same point, so that they cancel each other out. In such cases there are not two poles to the molecule and we say that it is non-polar. But it may happen that the centres of positive and negative charge are not coincident; there is a definite point where the negative resultant acts, and another point where the equal positive resultant acts. So the molecule is a little electric dipole and is called a polar molecule.

The turning effect of a force is measured by its moment,

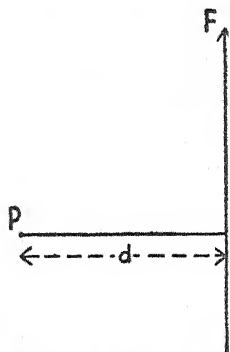


FIG. 18.—The moment of the force F about the point P is equal to $F \times d$.

that is, the product of the force and its distance from the point about which it is acting. This is a reasonable measure, since the greater the force and the greater its distance from any point the greater is its effect about that point. (This is the familiar idea of leverage. The farther out from the fulcrum a force is applied, the greater is the effect of the force you use.) There is a similar measure for the effect of the charges in a polar molecule; this is the product of the magnitude of either of the resultant charges and the distance between them. This measure is called the dipole moment. It is again a reasonable measure; the greater the charges and the greater their distance apart the greater is the dipole moment.

Consider the case of hydrogen chloride, HCl . The molecules of this substance are polar; when it is dissolved in water we get the ions H_3O^+ and Cl^- . The ions are distinct and separate entities that wander freely in the solution. There is here an obvious and distinct polarity, indeed a complete separation of positive and negative charges. It is in this ionised state that hydrogen chloride exhibits its well-known acid properties.

In the pure state, when it is quite free from water, hydrogen chloride is not ionised and it has none of its usual acid properties. It has no action on chalk, for example, which is surprising when one thinks of the rapid evolution of carbon dioxide when aqueous hydrogen chloride acts on chalk. But the charges are separated to some extent even in the un-ionised state, so that the molecule is polar; but there is not the complete separation observed in the ionised state. The dipole in un-ionised hydrogen chloride is due to the fact that the electrons in the chemical link are nearer the chlorine atom than the hydrogen atom, thus giving a preponderance of negative charge toward the chlorine atom; the positive pole of the dipole is toward the hydrogen atom.

In hydrogen chloride, then, we have in the ionised state the

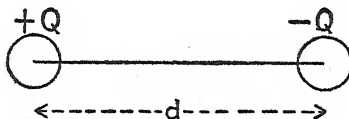


FIG. 19.—In an electric dipole the dipole moment is equal to $Q \times d$.

transference of an electron from the hydrogen to the chlorine atom; while in the covalent state there is only a partial transference, the electrons of the link are nearer the chlorine atom than the hydrogen atom.

In non-polar molecules the resultants of the positive and the negative charges act at the same point. This can happen only if the molecule has a fairly high degree of symmetry; indeed non-polarity often gives a clue as to the structure of molecules. The chlorine molecule, Cl_2 , is an example of a symmetrical, non-polar molecule. It is represented by

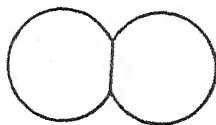
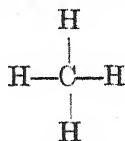


FIG. 20.—The chlorine molecule.

$\text{Cl}-\text{Cl}$; if we want a rough picture of the molecule we can think of two tennis balls pressed together. There is symmetry about the centre of the molecule and the resultants of the charges fall there. Hence there is no permanent polarity in the chlorine molecule.

The methane molecule, CH_4 , is another example of a non-polar molecule. The structure is:



The hydrogen atoms are at the corners of a tetrahedron with the carbon atom at the centre. (This is an arrangement similar to that of the carbon atoms in a diamond, except that the tetrahedrons are separate and not interconnected as in the diamond.)

The resultants of all the positive and of all the negative charges fall at the centre of the carbon atom. There is no observable dipole moment.

When one considers that unlike charges attract one another, it is only to be expected that an electrical field

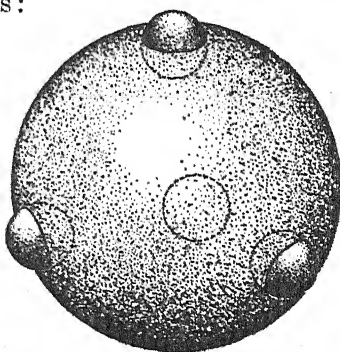


FIG. 21.—The methane molecule. The large sphere is the carbon atom; the bulges are the hydrogen atoms.

should have a distinct effect on the polarisation of molecules. It is not surprising to find that polarisation can be induced even in molecules that are normally non-polar. When non-polar molecules, such as those of chlorine, are subjected to an electric field there is a shift within the molecules. The negatively charged electrons are attracted toward the positive pole of the electric field; the positively charged nuclei are attracted toward the negative pole. The molecules thus acquire a temporary polarisation. This is comparable with the well-known phenomenon by which temporary magnetism is induced in a piece of soft iron by touching it with one of the poles of a magnet. The temporary polarisation disappears when the electric field disappears, just as temporary magnetism disappears when the magnet is removed.

The polarisation of a molecule can be measured, and although the methods of measurement may seem fantastic, they actually give trustworthy results. They usually involve the use of condensers. When an insulator (a dielectric) is placed between the plates of a condenser, the capacity of the condenser is increased. (This is a well-known phenomenon used, for instance, in the construction of condensers for wireless sets.)

We can now explain why a dielectric should increase the capacity of a condenser. The electric field of the condenser shifts the charges of the molecules of the dielectric, as already suggested—the negative charges toward the positive plate and the positive charges toward the negative plate. Some work is done in shifting the charges in this way; so if the dielectric is introduced into the condenser while its potential is kept constant, the condenser will now hold more energy than it did originally. It will have the original energy due to the charges on the plates plus the energy contained in the dielectric. When the condenser is discharged, the molecules revert to their normal state, their polarisation disappears, and all this energy is released.

Thus, for the same potential, the condenser can hold more energy with the dielectric between its plates than without the dielectric there. In other words, its capacity is greater.

In measuring the polarisation, first of all the capacity of the condenser is measured. It is then remeasured when the substance being tested (the dielectric) is between the plates. The ratio of these two capacities :

$$\frac{\text{Capacity with the dielectric}}{\text{Capacity without the dielectric}}$$

is the dielectric constant of the substance being tested. There is a mathematical relation between the dielectric constant and the total polarisation; this relation enables us to calculate the polarisation of a single molecule.

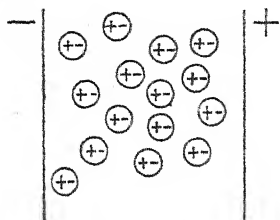


FIG. 22.—The deformation polarisation. Negative electrons are shifted toward the positive plate, and positive nuclei toward the negative plate. Each molecule becomes a small dipole.

The polarisation caused by an electric field is a composite thing; three different effects are entangled in one. The first two of these affect all molecules; the third affects polar molecules only.

(1) There will obviously be a shift within the atoms; the negative electrons are shifted toward the positive plate. This form of polarisation is often called the electron polarisation.

(2) There is a lesser effect due to the shifting of the positive nuclei toward the negative plate, sometimes loosely described as a shifting of the atoms within the molecule. This is called the atom polarisation.

These two effects together are the deformation polarisation, because they involve actual distortion of the molecule. Deformation polarisation affects all molecules in an electric field.

(3) The third form of polarisation affects polar molecules only. Each polar molecule in the field gets a twist, the negative pole toward the positive plate, the positive pole toward the negative plate. Each molecule is thus set more or less parallel to the electric field. For this reason this form of polarisation is called the orientation polarisation. The orientation is opposed by thermal motion, and is ordinarily

only very small. The molecules are in a continual state of agitation, which becomes greater and greater at high temperatures. This haphazard agitation jigs the molecules out of place, and at high temperatures it most effectively checks attempts at orientation.

What we actually want to measure is the permanent dipole moment of a molecule, and not the temporary (induced) effects. We get this from the orientation polarisation, which must be disentangled from the other two kinds of polarisation. There are several ways of doing this.

(1) The first method is more amusing than practical. In the solid state the molecules are so tightly packed that there

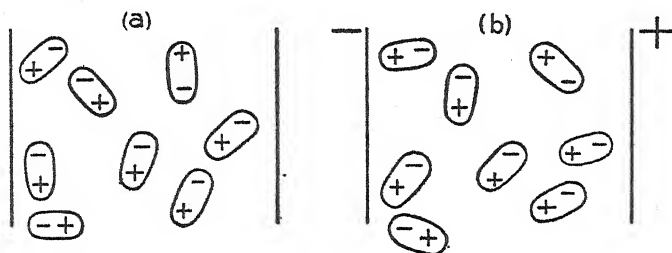


FIG. 23.—The orientation effect. When the electric field is applied each molecule receives a twist—all in the same direction.

is no orientation worth measuring; they cannot turn without colliding with one another and shoving one another aside. A measurement in the solid state gives the electron and atom polarisations only. In the gaseous state, on the other hand, there is ample room for orientation, and a measurement includes all three forms of polarisation. Subtraction gives the orientation polarisation.

(2) Another method is based on the fact that the deformation polarisation is not affected by changes in temperature, whereas the orientation of the molecules is affected. As the temperature is raised the thermal agitation becomes greater so that the orientation becomes less and less; the deformation polarisation remains constant. A graph enables the two to be disentangled.

[The equation is: $P = A + \frac{B}{T}$

P = the total polarisation (actually measured).

A = the deformation polarisation.

$\frac{B}{T}$ = the orientation polarisation at T° absolute.

P is plotted against $\frac{1}{T}$. XY is the resulting graph.

$ZW = A$, and (since $YW = P$) $YZ = \frac{B}{T}$

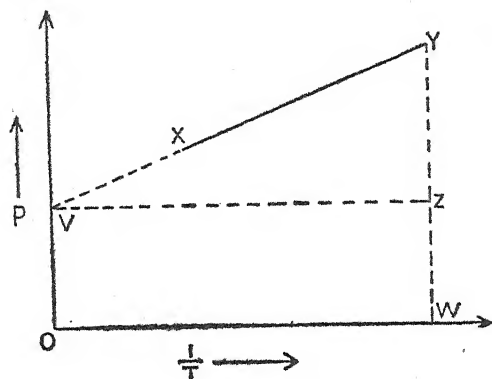


FIG. 24.

Hence the slope of $XY = \frac{YZ}{VZ} = \frac{B}{T} \div \frac{1}{T} = B$

That is, the slope of the graph gives the value of B .]

(3) The following method of disentangling the forms of polarisation is easily the most important of those used. It depends upon the application of an alternating electric field to the substance being tested.

Each alternation in the field is a switch over in polarity; the positive and negative poles of the field are interchanged at each alternation. If the molecules are polar, they get alternate twists in opposite directions. This sets them oscillating, swinging on axes as compass needles swing; although they would not usually swing right round. The

electrons also oscillate within the atoms in time with the alternating field, and the atoms of each molecule oscillate relatively to one another. These are the three forms of polarisation in a new guise; there is an oscillation corresponding to each kind of polarisation.

A preliminary measurement is made which includes all the three effects due to the oscillations of molecules, atoms, and electrons. Then the frequency of oscillation of the electric field is increased. The alternations become so rapid that the comparatively clumsy molecules can no longer keep pace with them; the tugs come so rapidly, one after another, that the molecules have no time to swing in one direction before they are tugged back in the opposite direction. So the orientation polarisation fades out and disappears. The measured value of the polarisation at this stage includes only the deformation effects due to oscillations of the atoms and the electrons.

At still higher frequencies the atoms give up the struggle to keep pace with the oscillating field and only the electronic oscillations are left. Finally they too die out, and at very high frequencies there is no observable polarisation.

The measurements actually made in the course of this determination are:

(a) A dilute solution of the substance in a non-polar solvent such as benzene is prepared*; the polar molecules are so far apart in the dilute solution that they do not interfere with one another. The dielectric constant of this solution is measured at radio frequency. (Radio frequencies are low, compared with those of ordinary light, though they are often called "high frequencies" in wireless.) The

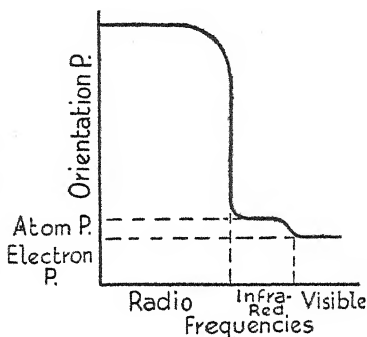


FIG. 25.—How the polarisation changes with frequency.

* This method can also be applied directly to gases and vapours.

dielectric constant gives the sum of the orientation and deformation polarisations.

(b) The refractive index of the solution is measured. The square of the refractive index gives the value of the dielectric constant at optical frequencies. (Ordinary light consists of electromagnetic oscillations of much higher frequencies than those used in wireless.)

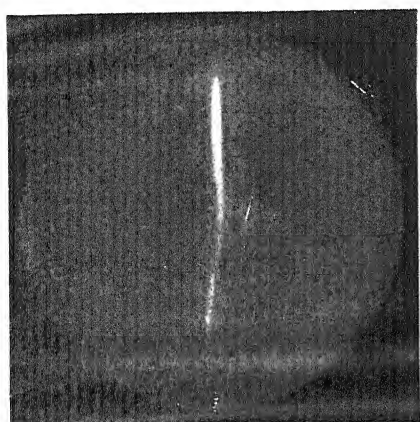
The radio-frequency measurement includes all three forms of polarisation. The optical frequency measurement includes the electron polarisation only. The difference includes both the orientation and the atom polarisation. The latter is small, and the error made by including it is not important. It is a pity, but it cannot be helped.

(4) To determine the dipole moment by the fourth method, we need a very tenuous beam of molecules of the substance to be tested; then we can investigate what happens when the beam passes through a very inhomogeneous electric field.

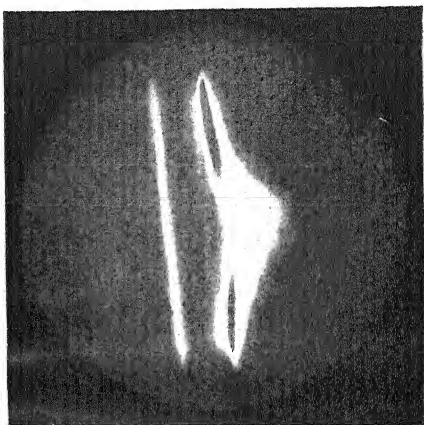
The substance is heated in a minute oven; the temperature is only just enough to give a very small vapour pressure; this gives the necessary tenuity. We have now to get a beam from the mass of molecules. The tenuous mass is allowed to stream through a narrow slit into a high vacuum; then the stream passes through a second narrow slit. A very narrow ribbon of molecules emerges; the molecules are so wide apart that there is no jostling and no spreading out. The beam falls on a brass plate kept cold by liquid air. When the molecules hit the cold surface they stay where they hit; they form a faint trace, which can be observed with a microscope.

The beam of molecules is now subjected to an electric field—a very inhomogeneous one. Suppose first that the molecules have no permanent dipoles. A dipole will be induced in each molecule by the electric field, and the dipoles will all point in the same direction, the direction of the field. Now the field is inhomogeneous, so that it exerts a different force on the two ends of the dipole. Each dipole gets a tug, and they are all deflected to the same extent; the trace on the plate makes a small shift as a whole.

PLATE III.



(a)



(b)

TRACES OBTAINED BY THE MOLECULAR BEAM METHOD.

(a) A trace from a non-polar substance: the trace is displaced but not broadened by the inhomogeneous field.

(b) The broadening of the trace from a polar molecule. The straight line is the trace obtained when the inhomogeneous field is not switched on.

(From Debye's "Dipole Moment and Chemical Structure." By kind permission of Messrs. S. Hirzel and Messrs. Blackie & Son, Ltd.)

If the molecules are polar, their dipoles are arranged haphazard. The electric field pulls them with varying force; those across the field, for example, get unequal tugs at both ends and are not deflected at all, those to their right the field get very unequal tugs at the two ends and are deflected the most. The beam of molecules is thus broadened, and of course, a shift of the trace as a whole, due to induced polarization. This occurs whether the molecules are positive or negative. The amount of broadening gives a measure of the dipole moment. (There is also, of course, a shift of the trace as a whole, due to induced polarization. This occurs whether the molecules are positive or negative.)

The fourth method is not so accurate as the others because the traces are faint and not easy to measure. It is sometimes applied when the other methods fail. This is the case with the alkali halides, which are thought to have large dipole moments. In the vapour state many of the

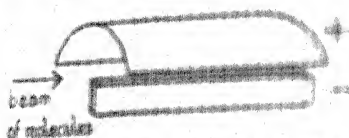


FIG. 26.—How the heterogeneous field is produced.

molecules of these substances consist of ions associated in pairs; there is a complete transformation of an electric force from one ion to the other. This accounts for the large dipole moment.

Besides these methods, which give fairly exact determinations of the dipole moment, there are others which can be used to give a rough indication of the size of the dipole moment, or to indicate merely whether a substance is polar or not.

The boiling point is often said to indicate whether molecules are polar, there is a stronger attraction between them than there is between non-polar molecules. The positive pole of one molecule attracts the negative pole of another, and they hold to each other like magnets. The stronger attraction between the molecules is overcome by thermal motion. For the same reason, polar molecules have higher boiling points than non-polar molecules. This effect is usually explained by a similar effect due to the weight of the molecules.

If the molecules are polar, their dipoles are arranged haphazard. The electric field pulls them with varying force ; those across the field, for example, get equal tugs at both ends and are not deflected at all ; those in line with the field get very unequal tugs at the two ends and are deflected the most. The beam of molecules is thus broadened, and so is the trace on the brass plate. The amount of broadening gives a measure of the dipole moment. (There is also, of course, a shift of the trace as a whole, due to induced polarisation. This occurs whether the molecules are polar or not.)

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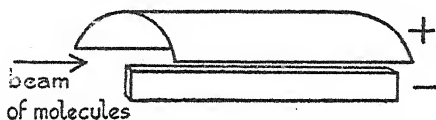


FIG. 26.—How the inhomogeneous field is produced.

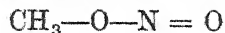
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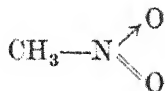
The boiling point is often such an indication. If the molecules are polar, there is a stronger attraction between them than there is between non-polar molecules ; the positive pole of one molecule attracts the negative pole of another, and they hold to each other like minute magnets. The stronger attraction between the molecules is less easily overcome by thermal motion. For this reason liquids with polar molecules have higher boiling points than those with non-polar molecules. This effect is usually mingled with a similar effect due to the weight of the molecules : the

molecules of a vapour are in rapid motion, and it is obviously more difficult to impart this motion to heavy molecules than to light molecules.

We can eliminate the complication due to the different weights by comparing a pair of isomers. Compounds are said to be isomeric when they have the same molecular formula—but, of course, the atoms are arranged differently in the two compounds. The difference in the boiling points of two such substances is due mainly to their having different dipole moments. Methyl nitrite, for example, has a boiling point of -12°C ., whereas the isomeric nitromethane boils at 101°C . The difference is explained by the structures of the two molecules. Methyl nitrite is :



and its dipole moment is small. Nitromethane has the structure :



The co-ordinate link (indicated by the arrow) involves the shifting of two electrons from the nitrogen atom toward the oxygen atom. For this reason the substance has a much higher dipole moment than its isomer, and consequently a higher boiling point.

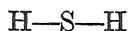
Another, and a simple, means of distinguishing between polar and non-polar molecules can be applied to liquids. The liquid is placed in a rotating electric field. The molecules of a non-polar liquid are not affected by the field, whereas polar molecules tend to follow the field round and so set the liquid in rotation with the field.

The measurement of dipole moments often gives interesting information about the structure of molecules. Carbon dioxide, for example, is non-polar. The only possible structure that will account for its zero dipole moment is the symmetrical linear structure :



and we accordingly conclude that this is the actual structure of the carbon dioxide molecule.

Hydrogen sulphide, H_2S (sulphuretted hydrogen) is polar. It cannot therefore have the symmetrical linear structure :



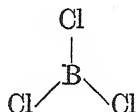
which would be non-polar. The actual structure is probably :



with a right angle between the links.

The case of carbon dioxide may be compared to two equal forces pulling in opposite directions ; they cancel each other out. The case of hydrogen sulphide corresponds to two forces pulling at right angles to one another, so that there is a resultant along the line bisecting the right angle.

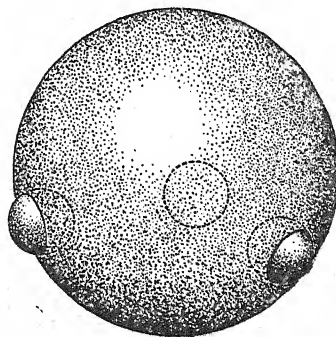
Boron trichloride, BCl_3 , is non-polar. This gives the structure :



All the atoms are in one plane, and the chlorine atoms are equally spaced around the boron atom. Any other arrangement would destroy the symmetry and produce polarity.

Ammonia, NH_3 , which also contains three atoms of one sort to one of another sort, is polar ; so its structure must be quite different :

FIG. 27.—The ammonia molecule. The larger sphere is the nitrogen atom; the bulges are the hydrogen atoms. It is instructive to compare this diagram with Fig. 58 (p. 164), another representation of the ammonia molecule.



The molecule is pyramidal in structure with the nitrogen atom at the apex.

There is an interesting group of isomers called cis-trans isomers. An example will explain this kind of isomerism :



In the cis-compound, that on the left, the hydrogen atoms are both on one side of the molecule ; in the trans-compound, on the right, the hydrogen atoms are on opposite sides. (The compounds are cis- and trans-dichloroethylene.)

The dipole moments of the carbon-chlorine links in the cis-compound have a resultant along the dotted line of symmetry ; so also have the dipole moments of the carbon-hydrogen links. As these two resultants are not equal the molecule is polar. In the trans-compound the dipole moments of the two carbon-chlorine links are equal and in opposite directions ; so are those of the carbon-hydrogen links ; in both cases they cancel out, so that the molecule is non-polar. An examination of the dipole moments is in this case the only sure way of distinguishing which is to be regarded as the cis- and which as the trans-compound.

CHAPTER XI

SOLVENTS AND SOLUTIONS

WATER is far and away the commonest of all liquids, so that we are inclined to think of it as typical of liquids in general. We are familiar with many of its properties and especially with its power of dissolving solids, so that we are apt to describe solids as insoluble when they do not dissolve in water even though they may be very soluble in other liquids. The property of dissolving other substances is so closely associated in our minds with water, and hence with liquids in general, that it is something of a surprise to find a whole class of liquids which do not dissolve, say, common salt, or dissolve it in minute proportions only.

That there are two classes of liquids which differ widely in properties is shown by the amounts of various substances which can be dissolved in water and benzene respectively. A kilogram of water will dissolve 361 grams of common salt, more than a third of its own weight ; but only 0.1 gram of naphthalene, the ten-thousandth part of its own weight. On the other hand, a kilogram of benzene will dissolve 708 grams of naphthalene, nearly three-quarters of its own weight ; but the amount of common salt it dissolves is too small to be detected, less than a millionth part of its own weight.

There is thus a striking difference in the solvent properties of water and benzene. These two liquids are, indeed, typical of the two main classes of solvents.

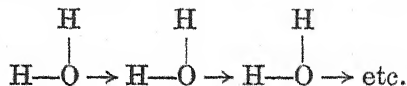
Water possesses in a highly developed form all the properties of its own class of liquids. The power of ionisation is one of the distinctive properties. Water ionises a large proportion of the substances which can be dissolved in it ; it is, indeed, the best of all ionising solvents. Benzene, on the other hand, never ionises the substances dissolved in it.

We saw in an earlier chapter how this difference in solvent properties can be used to distinguish between electrovalent and covalent compounds.

The two classes of liquids differ also in dielectric constants. Those of the water class have their dielectric constants high; those of the benzene class have low dielectric constants. The difference is a result of a difference in the dipole moments of the molecules of the two classes of liquids: those of the water class have high dipole moments; those of the benzene class have low dipole moments—benzene itself has a dipole moment of zero.

As a consequence of their high dipole moments the molecules of liquids of the water class attract one another strongly; much as two bar magnets attract each other. One result of the strong attraction between the molecules is that these liquids have abnormally high boiling points. Water boils at 100°C ., whereas benzene boils at 78°C . Yet water has a molecular weight of 18, compared with benzene's 78; so that we should have expected benzene to boil at the higher temperature.

Another theory has been put forward to explain the special properties of liquids of the water class. It is suggested that molecules of these liquids can polymerise, that they combine to form long chains. Water contains a donor atom, the oxygen atom, which has two lone pairs. It is possible, also, that the hydrogen atoms in water can act as acceptors. The hydrogen atoms have each two electrons in their valency group; if they can increase their valency group to four electrons they will be able to act as acceptors. If this is the case, then the water molecule is both a donor and an acceptor. The oxygen atom in one molecule can form a co-ordinate link with a hydrogen atom in another molecule, the second molecule may co-ordinate on to a third, and so on, until a whole series of water molecules are linked together in this way:



The links do not continue indefinitely; thermal agitation

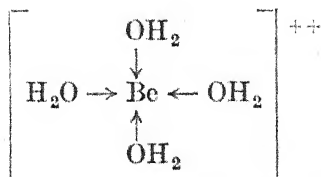
imposes a limit to the number of molecules which can be associated in this way. If long chains happen to be formed they are very likely to be broken up by collisions with other molecules. With increase of temperature the collisions became more frequent and more vigorous, so that the average size of the associated groups decreases.

All liquids containing the OH group are more or less abnormal in their properties, that is, they belong to the water class. Their abnormal properties may be explained in the same ways as those of water were explained. All liquids containing the OH group have high dipole moments: this is one possible explanation. Or, the molecules may be able to polymerise. According to the latter theory the OH group contains both a donor, the oxygen atom, and an acceptor, the hydrogen atom; all compounds containing the OH group should, therefore, be able to form chains in the same way as water. Anyway, whatever the explanation there is no doubt of the fact that liquids containing the OH group belong to the water class. The alcohols, for example, all contain the OH group and all belong to the water class of solvents [except those alcohols which contain a very long paraffin chain which swamps the effect of the OH group].

One of the special properties of the water class of solvents is the ease with which they dissolve electrovalent compounds. This is partly due to the high dielectric constant, a property common to this class of solvents. The chief factor which hinders the solution of electrovalent compounds is the powerful electrostatic attraction between the oppositely charged ions in such compounds. This attraction is reduced by the high dielectric constant of the water class of solvents—in the case of water itself by a factor of eighty. This permits the ions to wander about more freely, and the compound readily dissolves. The freedom of the ions is increased also by a protective sheath, consisting of molecules of the solvent, which forms round each ion. If two oppositely charged ions approach each other the protective sheaths serve to keep them apart. We have, then, two reasons why liquids of the water class should be able to dissolve electrovalent compounds: the high dielectric constant of the solvent, and the

formation of protective sheaths round the ions of the solute.

The protective sheaths about the ions are formed partly by means of co-ordinate links. We have to consider two kinds of ions: the positive ions (cations) and the negative ions (anions). The positive charge on a cation makes it a strong acceptor; the positive charge attracts the lone pairs of (negative) electrons on donor molecules. Let us see how this works out in the case of the beryllium ion, Be^{++} . This ion is a particularly strong acceptor because of its double positive charge, and also because of its small size. It has the helium configuration, (2). The neutral beryllium atom has four electrons; the ion has two positive charges, showing that two electrons have been lost; so that two electrons remain in the ion. Now if the ion were to receive eight more electrons it would have the neon structure, (2) (8). Hence it can form four co-ordinate links, with water molecules acting as donors:



This is the hydrated beryllium ion, usually written $[\text{Be}(\text{H}_2\text{O})_4]^{++}$. Other cations can be solvated in a similar way.

The solvation of anions is a more difficult and a more doubtful matter. The anions, being negatively charged, tend to act as donors rather than acceptors—they repel rather than attract electrons. If it is true—as already suggested—that the hydrogen atom can have a valency group of four electrons, then the hydrogen atoms in liquids of the water class can act as acceptors, and there is a possibility of anions being solvated. For example, the chloride ion, Cl^- , may be hydrated in this way:



But all these theories which ascribe to hydrogen the power

of forming a valency group of four electrons are a little speculative.

Returning to surer ground : the solvent molecules in the protective sheaths round ions are not all held by definite co-ordinate links. Some of these molecules are held to the ions simply because they are dipoles. (It may be remembered that molecules of solvents belonging to the water class have high dipole moments.) One end of the dipole must have the opposite sign to the ion, and must, therefore, be attracted by it.

Solvents of the water class are characterised by the strong attraction between their molecules ; molecules of solvents of the benzene class have very little attraction for one another. This difference has an interesting result. When two solvents of the benzene class are shaken up together they mix quite easily ; there is no reason why they should not do so. If, however, we shake up, say, water and benzene, the two liquids do not mix ; if they are allowed to stand, they separate out into two distinct layers. The water molecules have a strong attraction for one another ; they tend to congregate together and so "squeeze out" the benzene molecules. Finally, if we shake up, say, water and alcohol, which are both liquids of the water class, we get mixing again. All the molecules in such a mixture attract one another, so there is no tendency for two layers to be formed.

It is for much the same reasons that water does not dissolve naphthalene whilst benzene does. The molecules of naphthalene have no dipole moment, so they do not attract one another at all powerfully. The molecules can, therefore, wander about quite freely in benzene ; in other words, naphthalene is soluble in benzene. But if we try to dissolve naphthalene in water, the water molecules tend to squeeze it out just as they tend to squeeze out benzene molecules ; so naphthalene is insoluble in water.

CHAPTER XII

MOLECULAR SPECTRA

IN considering spectra we return again to quanta, those definite small "packets" of energy that are absorbed or emitted by atoms and molecules. When light falls on an atom (or a molecule), the atom can sometimes take up energy from the light-waves, and so reach a higher electronic level. Or it can give out energy in the form of light-waves, and so reach a lower electronic level. The difference in energy between the two levels, upper and lower, is always a single quantum of light-energy.

The size of the quantum is not always the same: it depends on the frequency of the light-waves in question. It is equal, indeed, to the frequency of the light-waves multiplied by a number known as Planck's constant. The frequency is represented by ν and Planck's constant is represented by h , so the quantum is equal to the product, $h\nu$. The quantum, as we have said, is equal to the difference in energy of an atom before and after it has absorbed or emitted light. If we call E_1 and E_2 the energies of the two energy-levels, then

$$E_1 - E_2 = h\nu$$

This is Einstein's equation. We have met it before in connection with the spectra of atoms—of hydrogen atoms in particular; in this chapter we shall see how it applies to the spectra of molecules.

The Bohr theory of the atom enables us to calculate the various energy levels E_1 , E_2 , and so on for the hydrogen atom. Combining these levels in pairs, we get a series of differences like $E_1 - E_2$; the Einstein equation shows that each one of these differences corresponds to a particular light-frequency; or, what comes to the same thing, to a particular colour. There are thus a number of light-fre-

quencies associated with the hydrogen atom. Similarly, there are a number of light-frequencies associated with every other kind of atom ; each kind of atom can be identified by means of the light-frequencies associated with it.

[There are some pairs of energy levels of an atom which do not "combine" according to the Einstein equation, and do not lead to the emission or absorption of light. Certain "selection rules" are known which enable us to tell which levels combine and which do not.]

An absorption spectrum is obtained by passing a beam of white light through the vapour of the substance under investigation. White light contains all frequencies of light within the visible region of the spectrum. The atoms or molecules pick out and absorb some of the light-frequencies ; they absorb those frequencies which correspond to a jump from one energy level to another. The light coming through the vapour, therefore, contains less of these particular frequencies than of the frequencies which are not absorbed by the vapour. The light is then spread out into a spectrum, the familiar band of colours seen in the rainbow : red, orange, yellow, green, blue, indigo, and violet. (This may be done by means of a triangular glass prism, for instance.) In the spectrum, all the light-frequencies are sorted out ; there is a line in the spectrum corresponding to each frequency (or colour). But certain frequencies have been absorbed by the vapour that the light has passed through ; these frequencies appear in the spectrum as dark lines.

The same sort of thing happens in the parts of the spectrum which are not visible—in the infra-red part on the far side of the red end of the spectrum, and in the ultra-violet region on the far side of the violet end. But here we cannot see the dark lines. In the ultra-violet and in that part of the infra-red region which is very near the visible part of the spectrum, we can photograph the spectra to make them visible. In the rest of the infra-red part of the spectrum we have to depend on the heating effect of the light.

There is only one way in which an atom can absorb energy from light : one of its electrons must jump to a higher energy level. For this reason atomic spectra are

relatively simple : there is a definite dark line corresponding to each electronic jump. [Though there is a fine structure and even a hyperfine structure beyond that ; the latter is due to the spin of the nucleus.]

Molecular spectra are much more complicated. When the energy of a molecule changes, three effects may be involved :

(1) An electron may jump from one orbit to another. This is the same effect as that which gives rise to atomic spectra.

(2) A molecule can vibrate. A molecule consisting of two atoms is rather like a dumb-bell ; the atoms can vibrate, in and out, along the shank of the dumb-bell. Thus a molecule possesses energy of vibration. This energy exists in quanta, just like the electronic energy ; we say that the vibration of the molecule is quantised. So the energy of vibration can change a definite amount at a time, as does the electronic energy.



FIG. 28.—The vibration and rotation of a diatomic molecule.

(3) A molecule can rotate. The energy of rotation also is quantised ; so that when a molecule changes its rotational energy it does so in definite small jumps. Each small jump means the gain or loss of a quantum of energy.

The molecule may possess another kind of energy, too—energy due to the movement of the molecule *as a whole* through space [translational energy, in fact]. This kind of energy is not quantised—like the electronic, vibrational, and rotational energy—but it can have any value. At the moment, however, this kind of energy does not come into the question : we shall consider only the internal energy of the molecule.

Of the three forms of internal energy, the electronic energy is largest. In an electronic jump, the change in the energy of the molecule may be some ten to a hundred times as great as a change in energy due to a vibrational change. The vibrational energy changes are again some hundred times as big as the rotational energy changes. Hence the quantum,

$h\nu$, is greatest for electronic energy changes and least for rotational energy changes. The frequency, ν , follows the same order (since h is a constant). We look, therefore, for the electronic spectrum amongst waves of relatively high frequency—those of visible light and in the ultra-violet part of the spectrum. The vibrational spectrum is found among the lesser frequencies of the near infra-red—a little way out from the red end of the visible part of the spectrum. And, finally, we find the rotational spectrum in the far infra-red—far out from the visible spectrum.

The rotational spectrum is the simplest kind of spectrum given by a molecule. It is unfortunate that it should lie so far out in the infra-red, as the difficulties of observation there are very great. The only sources which emit light in the far infra-red region are all very feeble; they emit very little light of the desired frequency. There are, too, very few substances which are transparent to light in this region, so there are considerable difficulties about prisms and containing vessels for the substances we are investigating. Another difficulty is that we cannot photograph the spectrum and so view it as a whole. We have to rely on the heating effect of the rays and measure the amount of heat energy point by point along the spectrum; even at the best we cannot obtain a continuous record of the spectrum.

In spite of these great difficulties, the far infra-red spectra of several molecules have been examined. The rotation spectrum of hydrogen chloride,

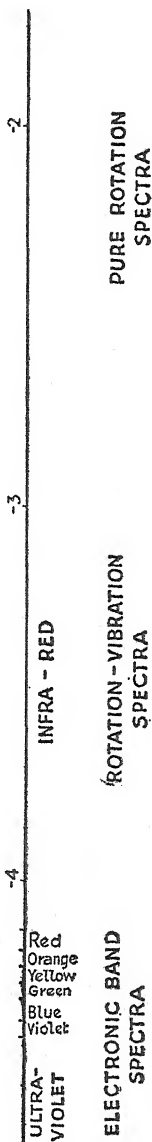


Fig. 29.—Where the various spectra occur. The scale is logarithmic (e.g. — 4 = 10^{-4} cm.).

for example, consists of a series of lines nearly equally spaced. From the positions of these lines we can calculate the distance between the hydrogen and chlorine atoms in hydrogen chloride or, more precisely, the distance between the nuclei of the two atoms [What we actually find directly from the spectrum is the moment of inertia of the molecule; this is connected by a simple mechanical formula with the distance between the atoms.] The distance measured in this way is in close agreement with that found by other means of measurement.

It is not every kind of molecule that gives a rotation spectrum. If the molecule has a dipole moment, it does give a rotation spectrum; whereas non-polar molecules do not. This is because light is electromagnetic in nature. When a polar molecule rotates, the electric field in the neighbour-



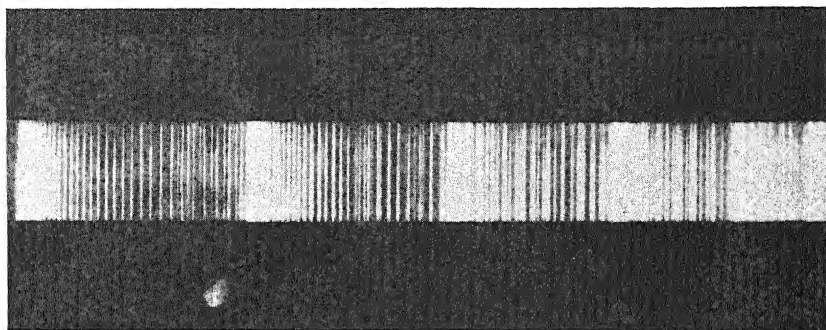
FIG. 30.—Diagram of a pure-rotation spectrum.

hood of the molecule is changing all the time; so a polar molecule can interact with light, it can change its rotational energy when light of the right frequency falls on it. We say that the rotational transitions of the molecule are "active."

But if the molecule is non-polar, its rotation is not an electrical phenomenon at all; the rotation cannot be increased by the absorption of the electro-magnetic energy of the light-waves. No absorption occurs, so there are no lines in the far infra-red spectrum of the substance in question; chlorine, for example, is non-polar and gives no far infra-red spectrum. This is not to say that a chlorine molecule does not rotate; only that its rotation cannot be affected by the absorption of light; its rotational transitions are "inactive."

The vibration spectrum, in the near infra-red, is much easier to observe than the rotation spectrum. But we get

PLATE IV.



BAND SPECTRUM (CYANOGEN BANDS).

(By kind permission of Mr. H. W. Thompson, St. John's College, Oxford.)

rid of one difficulty only to meet another. The trouble is that we seldom get vibrational changes alone; a change in the vibrational energy of a molecule is nearly always accompanied by a change in its rotational energy too. The spectra in the near infra-red are, therefore, not pure vibration spectra, but "rotation-vibration" spectra. A pure vibration spectrum would be a series of nearly equally spaced lines; the effect of the simultaneous change of rotational energy is to spread out each vibrational line into a band consisting of a series of fine lines close together; these fine lines form the "fine structure" of the band.

Imagine a case where the quanta of vibrational energy are 100 units and those of rotational energy 1 unit. There will be a central line in the spectrum corresponding to a pure vibrational change of 100 units. If the vibrational



FIG. 31.—Diagram of a rotation-vibration spectrum.

change is accompanied by one or more rotational changes, then the molecule will absorb light corresponding to energy changes of 99 and 101 units, 98 and 102 units, and so on. There will thus be a series of lines, which together constitute a band. The lines get weaker as we move away from the central line; so the band is not indefinitely broad.

Fig. 31 shows one of the rotation-vibration bands for HCl. The equal spacing of the lines is easy to see. The distance between successive lines gives us the difference in energy between two successive rotational levels of the molecule. But this is the same energy difference as that between two successive lines in the far infra-red spectrum. So we should expect the successive lines in a rotation-vibration band to be the same distance apart as the successive lines in the far infra-red spectrum; in each case the distance corresponds to a change of one quantum of rotational energy. This has been verified experimentally for hydrogen

chloride. We have here, therefore, a means of investigating the rotation of molecules without having recourse to the far infra-red, where observation is very difficult; in particular, we have a way of finding the distance between the atoms in a diatomic molecule.

It will be seen from Fig. 31 that the central line, the pure vibration line, is missing from the rotation-vibration spectrum of hydrogen chloride. This central line is actually missing from the near infra-red spectrum of every diatomic molecule (except that of nitric oxide, NO). This means that a change in the vibrational energy of a diatomic molecule does not take place, in the conditions which we are considering, without a simultaneous change in the rotational energy. Nevertheless we can readily find what position the line would occupy, because the other lines are spaced regularly about it.

The frequency of the central line enables us to calculate the force opposing the vibration of the molecule. The relative sizes of this force for the series of hydrogen halides are :

HF	HCl	HBr	HI
3.05	1.59	1.30	1.00

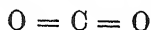
The force is strongest in hydrogen fluoride, HF, and weakest in hydrogen iodide, HI. This is in agreement with the experimental fact that hydrogen iodide is the most readily decomposed by heat and hydrogen fluoride the least readily. Heat causes the molecules to vibrate more violently; the link between the atoms is broken most easily when the force opposing vibration is least.

The vibration-rotation spectra of diatomic molecules are nowadays thoroughly understood. They are simple because the molecule can vibrate in one way only, in and out along the line joining the nuclei of the atoms. More complex molecules have several modes of vibration, and there is a corresponding complexity in their rotation-vibration spectra.

Triatomic molecules are the next simplest after diatomic, and they are at present the type that is being most extensively investigated by means of near infra-red spectra. One

question which has to be answered is : is the molecule in question linear, or is it triangular ?

Carbon dioxide, CO_2 , turns out to be a linear molecule :



This follows from two lines of evidence :

(1) The first line of evidence comes from the rotational fine structure of the rotation-vibration spectrum of carbon dioxide. It is found from this that there is only one kind of rotation of the carbon dioxide molecule that can give rise to the absorption of light. If the molecule were triangular, there would be three essentially different modes of rotation.

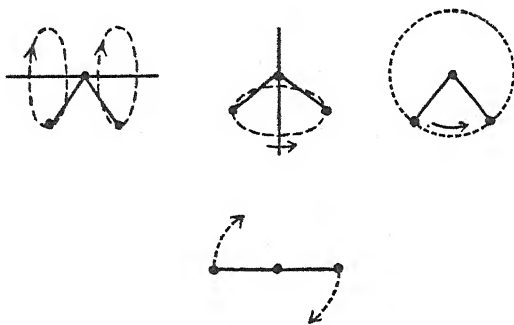


FIG. 32.—The three upper diagrams show the three ways in which a triangular triatomic molecule can rotate. Below is the single mode of rotation of a linear triatomic molecule.

[In more mathematical language, a linear triatomic molecule has one, and a triangular triatomic molecule three, moments of inertia which may be involved in the absorption of light-energy.]

(2) The linear structure of carbon dioxide is confirmed by examining how many essentially different modes of vibration of the molecule appear in the rotation-vibration spectrum. Any triatomic molecule has three modes of vibration. But in the case of a linear molecule like carbon dioxide, one of the modes of vibration is "inactive"; that is to say, it cannot give rise to any lines in the absorption spectrum.

For a mode of vibration to be active, to be able to lead to the absorption of light, the dipole moment of the molecule

must change during the vibration. This is the case with two of the vibrations of carbon dioxide (Fig. 33): the molecule is normally symmetrical and non-polar; during vibration it is distorted and polar, so there must be a change in its dipole moment. But during the remaining vibration (Fig. 33) the molecule remains symmetrical and non-polar throughout; there is no change in its dipole moment. So this kind of vibration of the molecule is inactive and does not give rise to any lines in the spectrum.

The electronic spectrum of a molecule is the easiest to investigate. It lies in the visible and ultra-violet parts of the spectrum, so that it can be investigated photographically, and the whole spectrum can be seen at once.

This ease of investigation is balanced by a complexity in

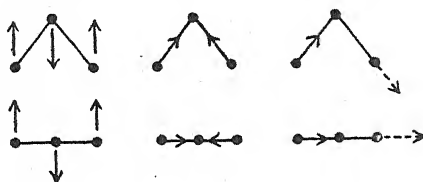


FIG. 33.—The upper diagrams show the three ways in which a triangular triatomic molecule can vibrate. Below are the corresponding ways for a linear triatomic molecule; the central one is inactive.

the electronic spectrum, much greater than that in the rotation-vibration spectrum. Each change in the electronic energy of a molecule may be accompanied by changes in both its vibrational and its rotational energy. Thus we have a very complicated spectrum. Instead of a line, each electronic transition gives a series of bands. Each of these bands corresponds to a particular change in vibrational energy accompanying the change in electronic energy; and each band has a fine structure due to simultaneous changes in the rotational energy. An imaginary case will make the matter clearer. Suppose that 10,000 units of energy are involved in the electronic transition, 100 units are involved in each vibrational transition, and 1 unit is involved in each rotational transition. Then there will be bands in each of the regions corresponding to 10,000 units, 9900 and

10,100 units, 9800 and 10,200 units, and so on. Each of these bands will have a rotational fine structure. For instance, the band with its centre at 9800 units will be accompanied by lines at 9799 and 9801 units, 9798 and 9802 units, and so on.

Actually the rotation lines are by no means equally spaced. (In the rotation-vibration spectrum, on the other hand, the spacing is very nearly constant.) Each band, as can be seen from illustration, has a "head"; the lines are crowded together at the head, which appears, therefore, as a sharp limit.

There is a series of bands corresponding to each electronic transition; each series contains many bands. In ordinary conditions, some dozen or half-dozen bands can be seen at once; others can be observed by altering the conditions. These band systems have many complications. The different systems often overlap; complex molecules are able to rotate and vibrate in more ways than one; some molecules dissociate into atoms or smaller molecules in the conditions of the experiment; there are further complexities due to the presence of isotopes. All these complications make the electronic spectra of molecules very difficult to interpret. On the other hand, once we can sort out the lines in the spectrum we can obtain information about all the factors giving rise to the complexities: we can use the electronic spectrum to measure the distance between the atoms in a molecule, to measure the forces in the links between the atoms, to detect what isotopes are present, and so on.

We have seen that such a non-polar molecule as oxygen, O_2 , gives no rotation or rotation-vibration spectrum. It might very well be thought that oxygen would give a simple electronic spectrum, free from rotational and vibrational complications—a series of lines like a simple atomic spectrum. It looks as though each electronic transition should give a single line—with presumably a fine structure like the hydrogen lines—instead of a series of bands.

Actually the oxygen molecule does give a series of bands, and the reason is this. When an oxygen molecule absorbs

energy and rises to a higher electronic energy level, it changes from a non-polar to a polar molecule. One of the electrons round one of the oxygen atoms has risen to a higher orbit than the normal; this electron is in a different orbit from the corresponding electron in the other atom. The molecule is no longer symmetrical; it has become polar. Thus the rotational and vibrational transitions of the molecule are no longer inactive; they may now be involved in the absorption or emission of light. So an electronic transition of the molecule may be accompanied by rotational and vibrational changes—just as with ordinary polar molecules. We get a series of bands corresponding to each electronic transition, and each band has a rotational fine structure. We can therefore study the rotation and vibration of molecules like oxygen by means of their electronic band spectra—a thing which cannot be done by means of infra-red spectra.

Molecular spectra are often diffuse and not banded at all; no definite lines can be distinguished in them. In some cases the bands get nearer and nearer together as the frequency of the light increases; eventually they merge into one another and we get a region of continuous absorption. In this region light of every frequency is absorbed, not merely a few definite frequencies. All this may seem remarkable. So far we have been accustomed to meeting quantised energy changes; such energy changes give rise to definite lines in the spectrum. The continuous absorption region indicates that the absorption of energy does not occur in sudden jumps, or quanta, but is a continuous process.

But why? Franck supplied the explanation. He supposed that the molecules begin to dissociate at the point where the continuous spectrum begins. Until this point is reached the atoms are connected by chemical links; vibration involves alternate stretching and compression of the links. So long as this goes on the vibrational energy must be quantised.

But a molecule may absorb so much energy from light falling on it that it breaks up into atoms—it dissociates. The actual dissociation uses up as much energy as it needs for the purpose; the rest of the energy becomes energy of

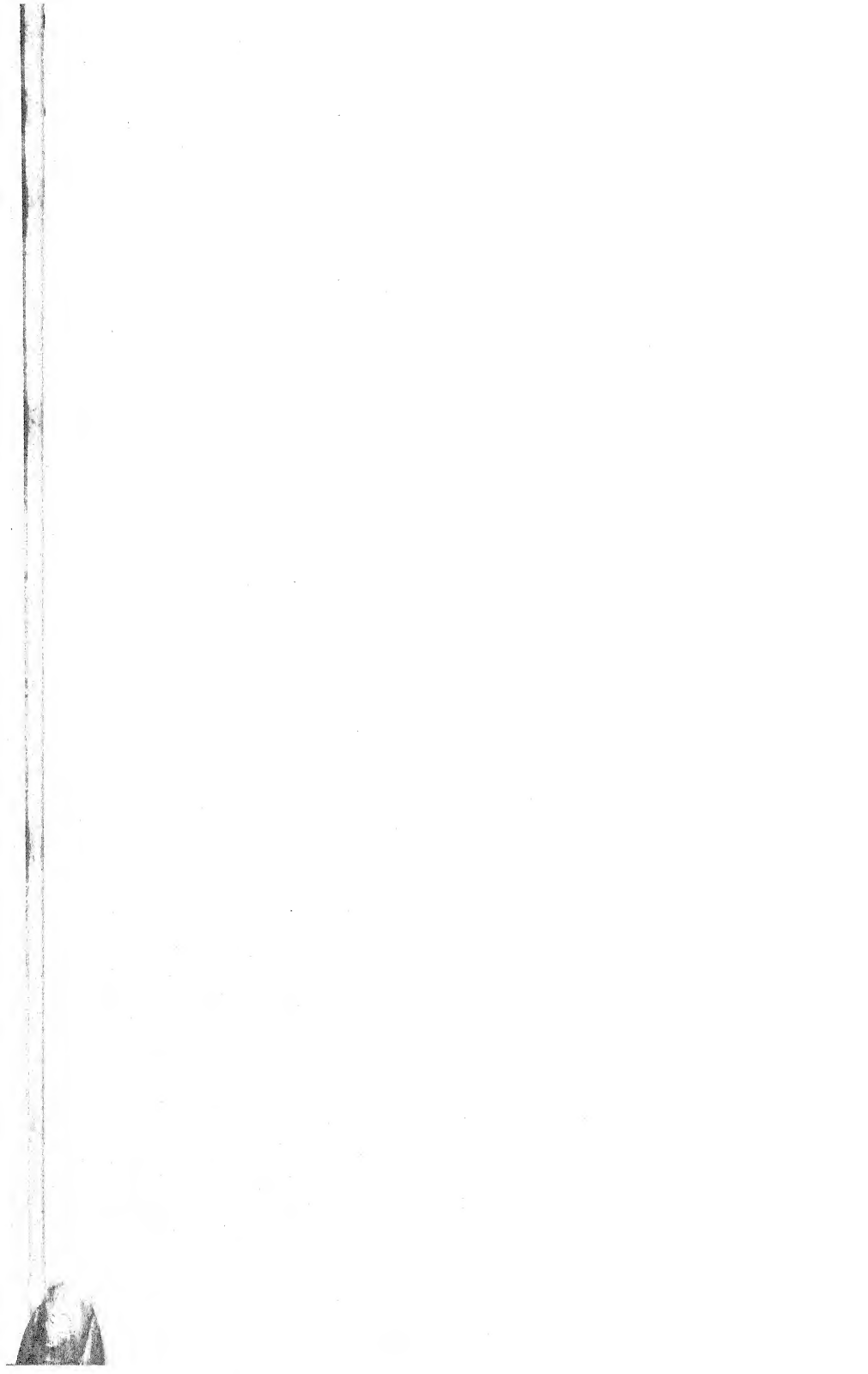
PLATE V.



CONTINUUM.

BANDS.

A series of bands leading into a continuum. The exact point in the spectrum where the bands end and the continuum begins cannot be found by direct observation ; the spectrum becomes too faint in this region. It is necessary to find, empirically, a mathematical law giving the positions of the bands ; we can then calculate where they merge into one another and the continuum begins. (*By kind permission of Professor W. E. Curtis, Armstrong College, Newcastle-on-Tyne.*)



motion of the separate atoms formed by the dissociation. The energy of motion (translational motion, from place to place, as opposed to vibration or rotation) can have any value at all; it is not quantised. Thus the total energy absorbed by the molecule can have any value above the minimum quantity needed simply to dissociate the molecule.

Now we know that every frequency in the spectrum is associated with an amount of energy $h\nu$. If we find the frequency, ν , at which the band spectrum ends and the continuous spectrum begins, we have found the energy necessary to break up the molecule into atoms. (We merely multiply the frequency by Planck's constant, h .)

We have thus discovered a way of finding the energy needed to dissociate a diatomic molecule like chlorine or oxygen. The atoms from the dissociated molecule are not usually, however, in their ground states. One of them is a normal atom; but the other is an excited atom, containing more energy than the normal; it is in a higher electronic state than the normal atom. Now the most useful quantity to know is the energy needed to dissociate the molecule into two normal atoms. To find this we have to subtract the energy used in exciting one of the atoms from the dissociated molecule. This method then gives a value for the energy of dissociation which can be compared directly with the value found by thermal methods. The spectral method is particularly valuable in the case of substances like oxygen, which can only be dissociated with difficulty. In such cases thermal methods are very difficult to employ.

RAMAN SPECTRA.—Raman spectra provide a remarkable example of the speed with which research in physical chemistry is being conducted. The first Raman spectrum was observed by Raman himself in 1928; during the next two years many hundreds of such spectra were obtained. Since then, however, there has been a distinct slackening off in the amount of work done in this field, largely because it is very difficult to interpret the experimental results.

Raman spectra are obtained by throwing a beam of light on to the compound examined; the light used is of one colour only, monochromatic. The light is scattered by the

compound. This scattered light is examined, by means of a spectroscope, from a point at right angles to the original (incident) beam of light.

A large proportion of the scattered light is found to be of the same frequency (that is, of the same colour) as the incident light: the molecules have neither given up energy to the light, nor taken energy from it. Some of the molecules do, however, absorb energy from the light. When this occurs the scattered light is of lower frequency than the incident light, that is to say, it lies nearer the red end of the spectrum. A few molecules actually give up energy to the light, in which case the scattered light falls nearer to the violet end of the spectrum than the incident light does.

As we know, a molecule absorbs energy in definite small amounts called quanta. For

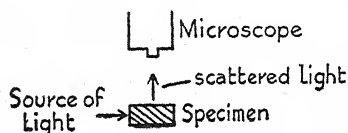


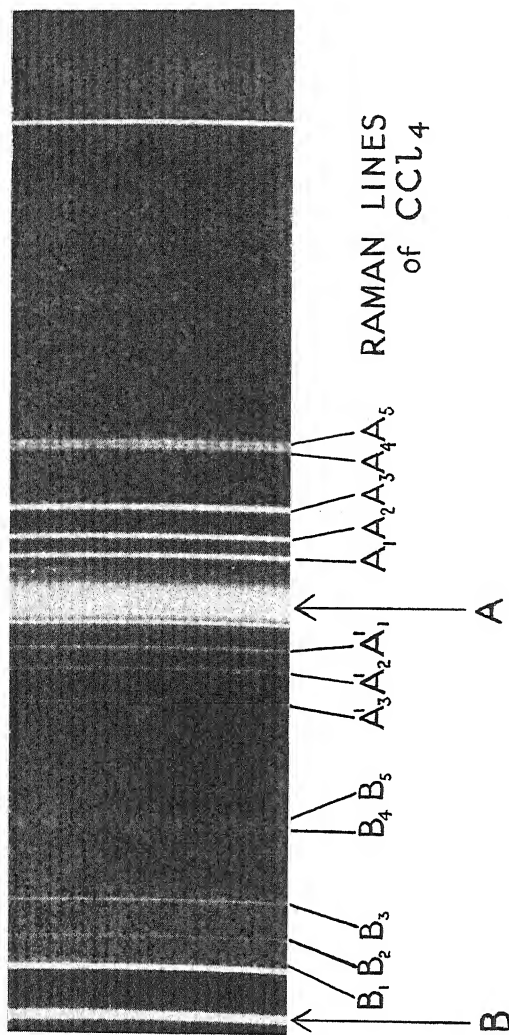
FIG. 34.—How Raman spectra are obtained.

this reason the Raman spectrum of a substance is found to consist of a series of lines. There is a very bright line of the same frequency as the incident light, and there is also a series of lines which fall

mainly on the red side of this line. The interesting point is to find the difference in frequency between the incident light and the scattered light: if we multiply the difference in frequency by Planck's constant, we get a measure of the amount of energy, the quantum, that has been absorbed by the molecule. The frequency difference is called the "Raman frequency." Each compound has a particular set of Raman frequencies associated with it, just as it has a particular set of lines and bands in its absorption spectrum.

The most easily observable lines in the Raman spectrum are those due to changes in the vibrational energy of the molecule; these vibrational changes are not accompanied by rotational changes. The Raman spectra of hydrogen chloride, and of other diatomic molecules, show the central line, the pure-vibration line, which is missing from the rotation-vibration spectrum. Many other inactive vibrations of a molecule, vibrations which do not give rise to lines in the

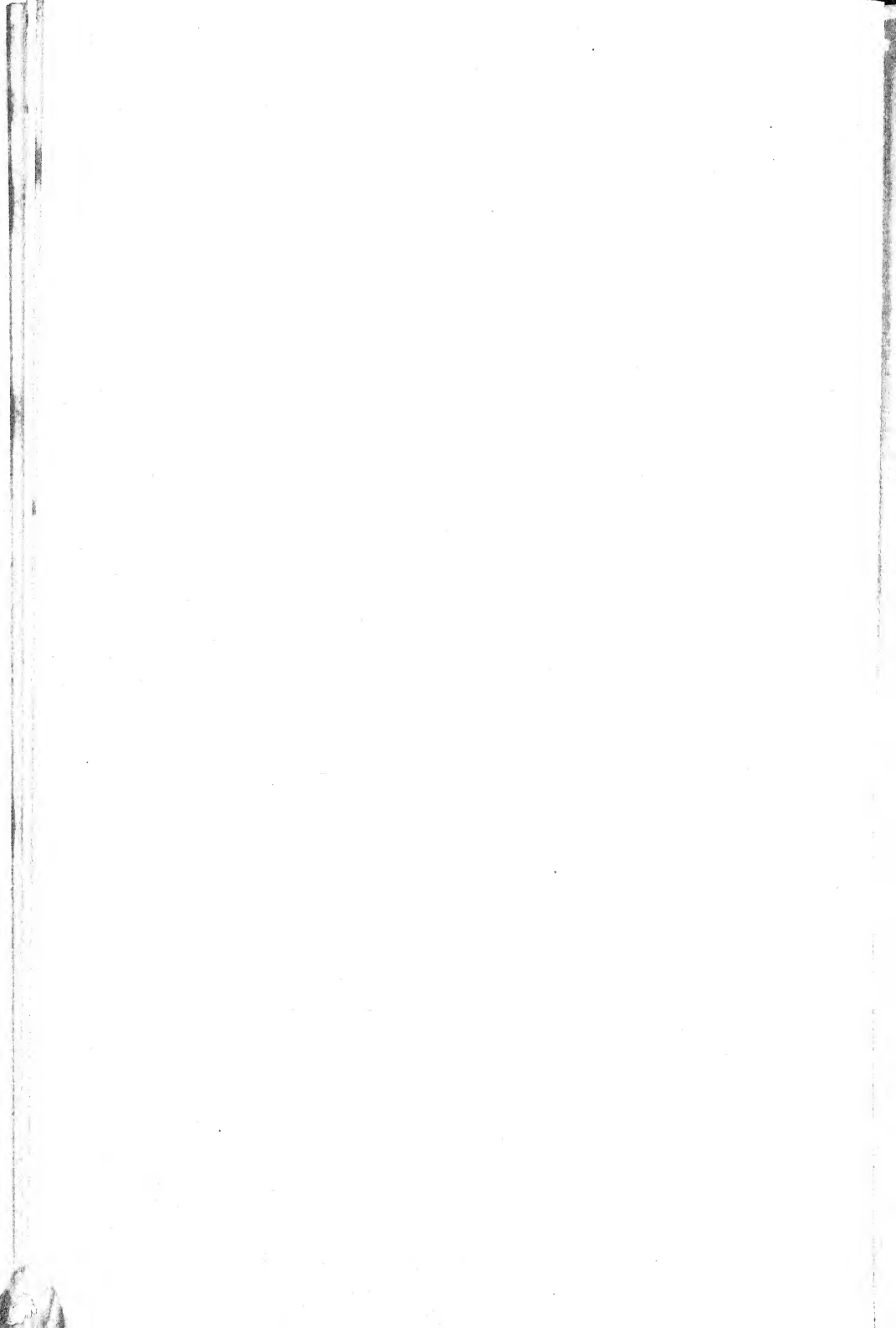
PLATE VI.



A TYPICAL RAMAN SPECTRUM.

The Raman spectrum of carbon tetrachloride. The incident light comes from a mercury arc lamp; it contains the bright lines marked A and B, besides a number of less important lines. Each of these lines, A and B, gives rise to a set of Raman lines, A_1 , A_2 , A_3 , A_4 , and A_5 ; and B_1 , B_2 , B_3 , B_4 , and B_5 . It is the change in frequency that is important, so the distance AA_1 is equal to BB_1 , AA_2 to BB_2 , and so on.

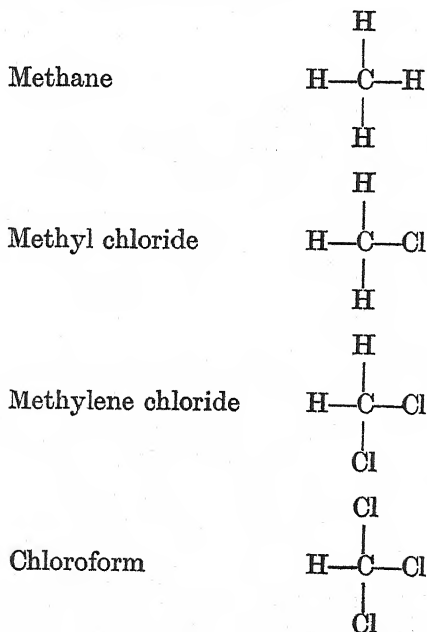
The lines A_1 , A_2 , and A_3 arise because a few molecules give up energy to the incident light instead of absorbing energy. Here again we have AA_1 equal to AA_1 , and so on. (By kind permission of Dr. L. A. Woodward.)

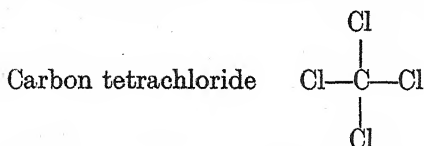


rotation-vibration spectrum, give rise to lines in the Raman spectrum. Chlorine, for example, gives no rotation-vibration spectrum, but it gives a Raman spectrum.

Raman spectra, then, give a valuable way of investigating the vibrations of molecules. The method is convenient because the Raman spectrum can be photographed, whereas the rotation-vibration spectrum falls in the infra-red and cannot be photographed. The method is particularly useful for the spectroscopic examination of relatively complex molecules. Such molecules cannot be investigated by means of their ordinary absorption spectra (either in the visible or in the infra-red part of the spectrum) because they decompose in the conditions which are necessary to obtain the absorption spectra.

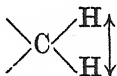
The vibrations observed by means of Raman spectra are really vibrations of the molecule as a whole. We may first assume, roughly, that the rate of vibration of any particular link in a molecule is unaffected by the other atoms present in the molecule. Thus in the series :





it will be seen that all the compounds except methane contain a C—Cl (carbon-chlorine) link. Corresponding to the vibrations of this link we find that there is a line in much the same place in the Raman spectra of all the compounds except methane. The line is not in exactly the same position for each compound ; but it is near enough to be identified.

Similarly there is a line corresponding to vibrations of the C—H link. This line can be identified because it is present in all the series of compounds except carbon tetrachloride, CCl_4 . Another line is present in all except CHCl_3 and CCl_4 ; this line is due to the >CH_2 group. The two valencies of the >CH_2 group can bend backwards and forwards



and this vibration gives rise to a Raman line.

It is apparent that Raman spectra are able to throw light on many problems of structure and of molecular mechanics.

CHAPTER XIII

CRYSTALS

It may seem strange that so many substances should have a crystalline structure: as though there were some urge toward regular geometrical form. Large crystals are clearly and obviously geometrical; and there are innumerable microcrystalline substances—things which are apparently amorphous, with no particular shape at all—that reveal their geometrical form when viewed under a microscope.

There are various ways of making crystals. Iodine crystals are formed by condensing iodine vapour; sulphur crystals, by allowing molten sulphur to solidify; crystals of alum, common salt, etc., by evaporating down and cooling their solutions; and so on. Even amorphous solids sometimes gradually become crystalline after, perhaps, several years; it is this process, called devitrification, that makes old glass opaque.

To obtain crystals of a large size, they must be allowed to form slowly, by slowly cooling a solution, for instance. If they are formed rapidly the molecules do not have so much time and opportunity to take up the regular crystalline form. This slow cooling is particularly important in the case of substances that crystallise only with difficulty. Stearic acid, for example, has long flexible molecules. When liquid stearic acid is cooled the molecules flop about and they usually finish up as a mass of entwined molecules forming a wax. Very slow cooling is required to give these flopping molecules the chance to fit into place side by side in an orderly crystalline arrangement.

The regular form of crystals is due to the regular arrangement of the molecules. In amorphous material the molecules are haphazard, anyhow, like a disorderly rabble. In the crystalline form they have the discipline of regiments on parade.

In common salt, sodium chloride, the molecules are particularly simply arranged. In solution, sodium chloride separates into positive sodium ions and negative chloride ions. This separation persists in the crystal; there are no neutral NaCl molecules present. But there is this difference between the solution and the crystal: in the former the ions have no special arrangement; in the latter they are arranged regularly. Each sodium ion has six chloride ions

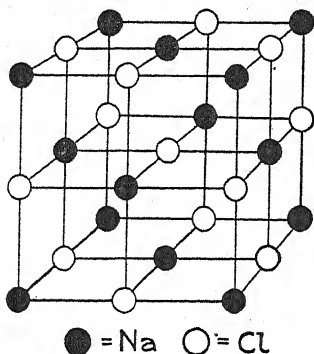


FIG. 35.—The "face-centred" lattice of sodium chloride.

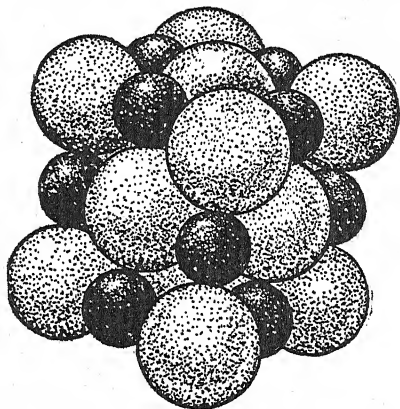


FIG. 36.—Another representation of the sodium chloride lattice. (After Wyckoff's *Structure of Crystals*, by permission of the Chemical Catalog Co., New York.)

arranged symmetrically around it, and similarly each chloride ion has six sodium ions round it; Figs. 35, 36 show how this arises from an arrangement of sodium and chloride ions alternately in a cubic lattice. (Of course, there are just as many sodium as chloride ions.) The symmetry of the arrangement ensures that there is no net attraction on any of the ions; each of the six negative chloride ions attracts the central positive sodium ion, but these attractions cancel one another out in pairs.

When a substance crystallises it generally tries to pack itself into the least possible space, thus giving what is called a close-packed structure. The ions in sodium chloride are roughly spherical; the chloride ions are considerably larger than the sodium ions—so they pack into the arrangement

already described. This arrangement is spoken of as the face-centred cubic lattice. It is so called because any ion is at the centre of one of the faces of a cube with four ions of the opposite kind at the corners of the face.

Cæsium chloride, CsCl , differs from common salt in that the cæsium ion is much larger than the sodium ion, and is very nearly equal in size to the chloride ion. Consequently the face-centred cubic lattice is no longer the most closely packed arrangement of the ions. Instead, cæsium chloride has a cube-centred cubic lattice. Each

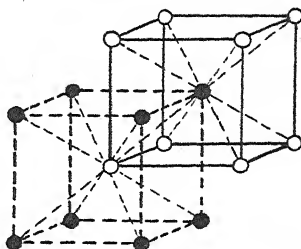


FIG. 37.—The "cube-centred" lattice of cæsium chloride.

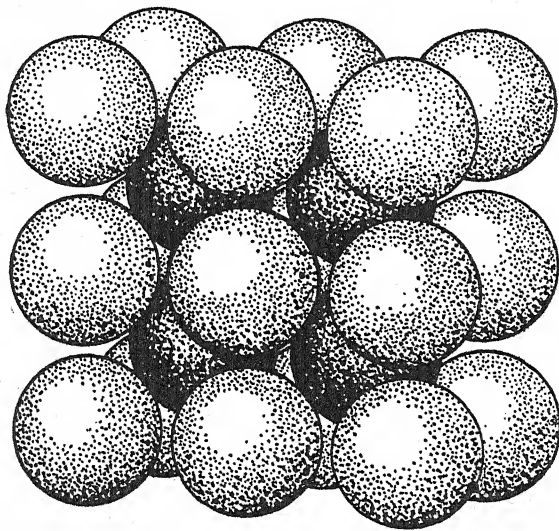


FIG. 38.—Another representation of the cæsium chloride lattice. (After Wyckoff's *Structure of Crystals*, by permission of the Chemical Catalog Co., New York.)

cæsium ion has a group of eight chloride ions round it, at the eight corners of a cube with the cæsium ion

at the centre. Similarly each chloride ion is surrounded by eight caesium ions. The name "cube-centred" is used for the lattice because each ion is at the centre of a cube with eight ions of the other kind at the corners.

The arrangement of ions and molecules in the crystal depends on the relative sizes of the different units of the crystal, and on their shape. If the shape of these units changes, on changing the temperature for instance, the crystal lattice will usually change as well; for a new packing may be more economical than the old. When a substance can exist in more than one crystalline form it is said to be polymorphic.

Ammonium nitrate presents an interesting case of polymorphism. This substance has no fewer than five different crystalline forms. It is a compound of the two ions NH_4^+ (the ammonium ion) and NO_3^- (the nitrate ion). Below -50°C ., neither of the ions rotates; both are fixed, and the crystals are rhombic in shape. At -50°C ., the ammonium ion begins to rotate and becomes effectively spherical in shape. In this form it takes up more room, and the crystals assume a different rhombic form. This form is retained until the temperature is raised to 32°C . Here there is another change of shape to the form known as monoclinic. The nitrate ion then begins to rotate. The nitrate ion, NO_3^- , consists of a central nitrogen atom with three oxygen atoms symmetrically around it, in the same plane. It begins to rotate about the central nitrogen atom, and so takes the shape of a disc. In this range the crystals are tetragonal in form. At 125°C ., the kind of rotation of the nitrate ion changes; it rotates quite freely in space and becomes effectively spherical. Above 125°C ., both ions are effectively spherical (as in sodium chloride) and the crystals are cubical.

THE GROWTH OF CRYSTALS.—Crystals generally need a nucleus to form on, such as a speck of dust or better still a minute crystal of the substance itself. The reason for this is that substances very finely divided are more soluble than usual; it would be difficult for a crystal to start without a

nucleus, therefore, because the first infinitesimal particle would simply dissolve again.

Usually, of course, there are sufficient nuclei present in the form of dust particles, etc., for crystals to form. But we can filter a solution free from particles that might serve as the nuclei of crystals, and then cool it down. In the ordinary way, crystals of the solute would be formed; but we have prevented this happening, so the solution becomes "supersaturated"—it contains more of the solid than is normally soluble at that temperature. This condition is readily upset; the addition of a single minute crystal of the solute brings down a whole mass of crystals at once.

If we go on cooling the solution after it has become supersaturated, crystals will eventually form even without the addition of any nuclei to it. As we cool the solution thermal agitation becomes less and less, so that any molecules which happen to get into the right relative positions for crystal formation are more likely to stay there whilst other molecules are arranging themselves about them. As soon as a tiny crystal has been formed in this way, the remainder of the solution crystallises at once.

The importance of crystallisation nuclei was illustrated in an amusing way in the case of cinnamic acid. Cinnamic acid exists in several polymorphic forms. Workers in different laboratories were often unable to reproduce results obtained in other laboratories, so that all the results were of doubtful value. This was because laboratories had become inoculated with traces of the first polymorphic form produced there. These traces acted as nuclei of crystallisation whenever crystals of cinnamic acid were prepared, and of course the whole crop of crystals was of the same form as the nuclei on which they had grown. If small crystals of all the polymorphic forms are available, we can produce any form at will by inoculating the solution with a small crystal of that form.

The best crystallisation nuclei are small crystals of the substance itself. When a solid is melted or dissolved in a liquid, a number of minute crystals persist for some time and can act as crystallisation nuclei. They are too small to

be visible even under the microscope, but their existence is demonstrated by the following experiment. A solid is heated just above its melting-point and then cooled again; it crystallises quite readily. If, however, it is heated well above the melting-point, the last minute nuclei of crystallisation are broken up by thermal agitation. On cooling the liquid again to the melting-point it does not crystallise at once, but must be considerably supercooled before a solid separates out.

The crystallisation nucleus is the foundation on which the crystal is built; the subsequent growth occurs layer by layer on this foundation. Think of a small crystal suspended in a solution; it may start for example as a small cube. The faces are all equally exposed to the solution and there is no reason why one face should grow quicker than another; molecules attach themselves as readily to one face as to another. The result is equal growth on all faces, and the persistence of the cube form. Growth on some sides may be checked if, for example, the crystal starts growing on a solid surface; the regular form is then preserved by the exposed sides only.

The reason why growth occurs equally along all the cube faces of, say, common salt is that those faces are all alike; each contains a network of alternate sodium and chloride ions. But suppose we consider a face formed by cutting away a corner of the cube—an octahedral face. This face will be quite different from the cube faces; it will in fact consist entirely of one kind of ion, instead of two kinds arranged alternately. In the case of sodium chloride the cube faces grow preferentially to these octahedral faces, to their complete exclusion as it happens. With some crystals, the cube faces are completely suppressed and shrink to a mere point; we then get an octahedrally shaped crystal. But the arrangement of the molecules in the interior of the crystal is essentially the same, whether it is cubic or octahedral.

Sometimes the preference for growth on particular faces is very striking. Crystals of mercury are formed by condensing mercury vapour at -10°C. on to a surface cooled

to -63°C . The crystals consist of small hexagonal plates, each about ten thousand times as wide as it is thick !

The growth of a crystal face occurs layer by layer. Each new layer starts at a corner or an edge of the crystal and then spreads over the face with great rapidity. The fact that each new layer starts at the edges and travels inwards keeps the edges sharp while crystals are growing. But when crystals are going into solution the edges become rounded because the edges go into solution first. This difference is used as a means of measuring solubility. The substance being tested is dissolved until only one small crystal is

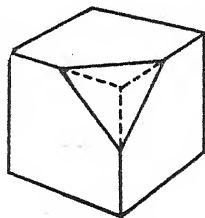


FIG. 39.—An octahedral face obtained by cutting away a corner of a cube.

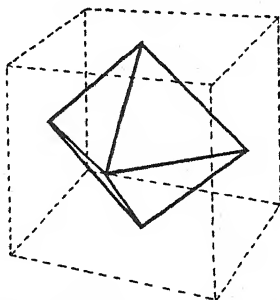


FIG. 40.—An octahedral crystal, showing how it is related to a cube.

left. By lowering or raising the temperature the crystal can be made either to increase or decrease in size. Which of these two is happening is shown by the appearance of the edges of the crystal. If we start with a weighed amount of solute we can find the exact temperature at which the last small crystal is just going into solution, and so find the solubility at that temperature.

The speed at which a crystal face grows thus depends on the probability of a new set of atoms being arranged in proper order along an edge or at a corner. The speed depends also on the nature of the face itself. If a new layer cannot spread rapidly over the face, then that face will grow slowly. Now it is a surprising fact that faces of slower growth increase in area at the expense of quicker growing faces.

This is due to the following circumstances: the small face ABC may be a fast-growing face compared with the faces DABE, etc. New layers form on the face ABC one after another until eventually it has shrunk to a mere point. The slow-growing faces have meanwhile increased in area.

The spreading of a new layer across a crystal face can be prevented if there is some impurity adhering to the face. Quite often an impurity will adhere to one face of a crystal but not to another. If it adheres to a normally fast-growing face, that face may become a slow-growing face, and so tend to increase in size.

By deliberately introducing a small amount of some impurity we can sometimes change the crystal habit of a substance. Thus rock salt, sodium chloride, normally crystallises in cubes. But when urea is present in the solution it adheres to the small faces at the corners of the cubes. These small faces grow at the expense of the cube faces, and the salt crystallises in octahedra. Another example is found in the case of ammonium sulphate. Ammonium sulphate is

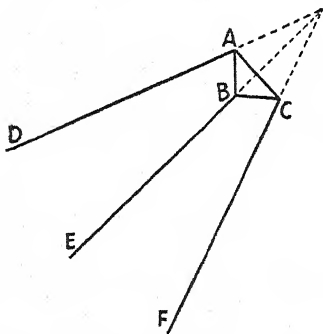


FIG. 41.—The small face ABC grows quickly and soon shrinks to a point.

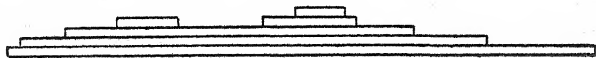


FIG. 42.—The appearance of a smectic liquid on a microscope slide.

an important fertiliser; it crystallises either in plates or in needle-like crystals. It is slightly deliquescent, and tends to cake together in a solid mass; the plate-shaped crystals stick together much more than the needles owing to the greater area of contact between them. This tendency to cake together is troublesome—the caked mass must be broken up before it can be spread on the land—so the

manufacturer wants to make the needle-shaped rather than the plate-like crystals. A trace of an iron salt will ensure that this kind of crystal comes out of solution, because the iron checks the growth of certain crystal faces.

LIQUID CRYSTALS.—When an ordinary solid melts it gives a clear liquid, provided of course that it is pure. But there are a few solids which melt to give cloudy liquids, and no amount of purification will make them give clear liquids. On heating the cloudy liquid some twenty degrees higher the cloudiness clears away quite sharply and an ordinary liquid is produced.

The cloudy liquids are called crystalline, or anisotropic liquids. They are like liquids as far as their mobility goes, but their optical properties resemble those of crystals.

There are two important classes of anisotropic liquids. (It is said that eighteen forms are possible in theory.) The first is known as the smectic class. The molecules of liquids of this kind have a remarkable tendency to group themselves into flat sheets, which can slide over one another. This is readily shown by carefully spreading the liquid on a microscope slide and examining it under the microscope; the liquid is seen to consist of a number of extremely thin layers one over another. There is very little cohesion between the layers; the lightest flick with a feather sends them skidding over one another. (Fig. 42.)

Substances which form anisotropic liquids always have long or flat molecules. In a smectic liquid the molecules tend to arrange themselves in layers parallel to one another, like corn in a field; so that little, plate-like crystals are formed. In the solid crystal, these layers are arranged regularly one above the other so that the whole structure possesses a definite shape. When the solid melts to an anisotropic liquid, the cohesion between the layers is no longer

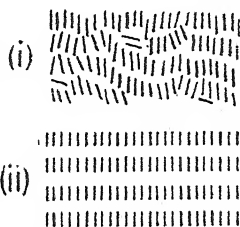


FIG. 43.—(i) The molecules in a smectic liquid, showing how they tend to group themselves into little crystals. (ii) How the molecules are arranged in the solid that gives rise to the smectic liquid on melting.

powerful enough to keep them in position one above the other. But the layers themselves, the individual liquid crystals, still remain more or less intact; that is why the smectic liquid has some of the properties of crystals, and why it appears as it does under the microscope.

The tendency of the molecules to group themselves into little platelets, is opposed by thermal agitation. If we focus attention on any particular platelet, it is soon broken up by collisions; the molecules of which it was composed then group with other molecules to form new platelets, and so the process goes on.

In the second kind of anisotropic liquids, the molecules still have a tendency to lie parallel to one another, but there is no tendency to form layers. (In an ordinary liquid the molecules are completely at random.) This is what we might have expected from a study of the solid crystals

formed by substances of this sort; the molecules in the solid are arranged parallel to one another, but they interleave so that there are no definite layers of molecules. The tendency to interleave persists in the anisotropic liquid produced when the solid melts.

If a thin layer of an anisotropic liquid of this sort spreads on a glass surface, the molecules next to the glass surface will be held fairly rigidly in position. The molecules above will then try and arrange themselves parallel to the molecules on the surface. If the glass is suddenly moved, the direction of the molecules on the surface will be different from the direction of those above; so the liquid assumes a twisted structure, full of vortices and intertwinings. This sort of structure has led to the term nematic (that is, thread-like) for this class of anisotropic liquids.

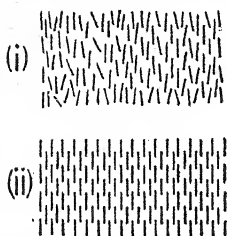


FIG. 44.—(i) The molecules in a nematic liquid, tending to arrange themselves parallel to one another. (ii) The solid from which the nematic liquid is derived. The layers of molecules interleave with one another.

CHAPTER XIV

X-RAYS AND CHEMISTRY

LIGHT consists of waves. Different kinds of light differ in wavelength, that is, in the distance from crest to crest of the waves ; differences such as those of colour are due to these differences in wavelength. Our eyes respond to light only when it is of suitable wavelength. On one side of the range of visible light there is light whose wavelength is too short for us to see it ; on the other side there is light whose wavelength is too long. But there are ways of detecting these waves that do not affect the eyes. They may, for example, affect a photographic plate, or we may be able to detect them electrically, as is the case with wireless waves.

X-rays are light-waves of wavelength which is far too short to affect the eyes.

They have certain properties which are now familiar to us all. They are able to

penetrate many materials which are opaque to ordinary light ; they penetrate flesh, for example, so they are of great importance in surgery. Fortunately they affect a photographic plate, so that they are relatively easy to observe and measure.

(The diagram on p. 287 shows the position of X-rays in relation to other kinds of light.)

X-rays are produced whenever atoms are struck by fast-moving electrons. In order to produce them we need a source of electrons and a suitable target (see diagram above).

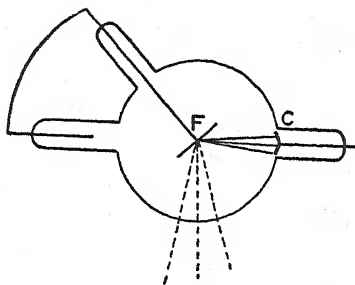


FIG. 45.—An X-ray tube. Electrons from the cathode C strike the target F, which then emits X-rays.

In the Coolidge type of X-ray tube the electrons are supplied by an incandescent tungsten wire; they fall on to a "target" or "anticathode" of a suitable metal, and the target then emits X-rays. The tube must be evacuated. The electron stream is maintained by making the filament negative and the target positive, so the (negatively-charged) electrons tend to pass from the filament to the positively-charged target. [It is not actually necessary to use a direct current to run the tube. The unrectified high-tension output of an ordinary step-up transformer can be used instead, the tube acting as its own rectifier.]

One of the most important uses of X-rays is in the study of the structure of crystals.

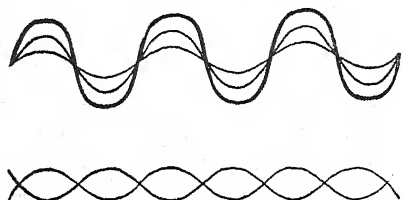


FIG. 46.—The upper diagram shows how waves reinforce one another when in phase. The heavy line shows the wave produced by the combination of the other two. The lower diagram shows how two waves cancel one another out when one is half a wavelength behind the other.

Most of the knowledge of crystal structure that has been assumed in the chapters on crystals and on giant molecules is derived from X-ray investigation. Our knowledge that sodium chloride has a cubic lattice, for example, is derived by the use of X-rays.

Before enquiring into the methods of investigating crystal structures, we must consider a phenomenon known as interference, which is common to all kinds of light.

Light is, as we have said, a wave-motion. Now what will happen if two such waves are superposed? It may happen that the crests of one wave coincide with the crests of the other, and the troughs with the troughs. When this occurs the waves are said to be in phase. It is easy to see that the waves will reinforce each other; we shall get a new wave with crests higher than those of either of the original waves, indeed equal to their sum.

If, however, the crests of one wave coincide with the troughs of the other, then the effects of the two waves will

cancel each other out ; the two wave-motions are " out of phase."

When two light-waves interfere like this, then, they may either reinforce or oppose one another. In the former case the light appears more intense, brighter. In the latter case we may get complete darkness, or at any rate a diminution in intensity. This is just as true of X-rays as of visible light, except that the interference of X-rays cannot be detected by eye, as can that of visible light.

In every crystal there is an ordered array of atoms and molecules. In what follows, we shall see how X-rays can be used to elucidate the nature of this array.

When a beam of X-rays falls on a crystal, each atom in the crystal scatters (diffracts) in all directions the X-rays that fall on it. What we have to consider are the conditions that rays diffracted by adjacent atoms shall be in phase. For this to happen, the X-rays from one atom must " get ahead " of those from the adjacent atoms by a distance equal to

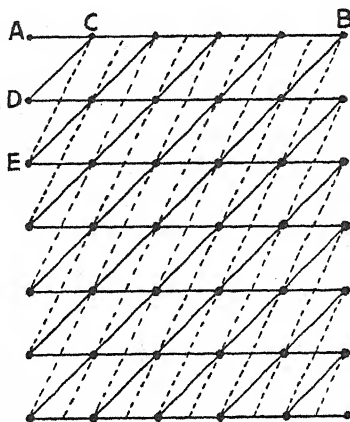


FIG. 47.—A 2-dimensional network of atoms.

one wave-length of the X-rays. The reason why this often happens is simply that the wavelength of X-rays is about equal to the distance between adjacent atoms in the crystal ; visible light, with its much longer wavelength, would be far too clumsy.

In order to simplify matters, we will consider first a two-dimensional network of atoms ; it will readily be seen that the same principles apply to the three-dimensional lattice of a crystal. The atoms in the two-dimensional lattice may be considered as lying in a series of lines parallel to AB ; or they may be considered as lying in a series of lines parallel to CD ; or parallel to CE, and so on. It is obvious that a

large number of different line groupings of the atoms are possible. In just the same way, the atoms in a three-dimensional lattice may be grouped into parallel planes, and there are many ways in which this grouping can be carried out. Not all these ways are equally important; some of the possible planes contain very few atoms, and are relatively unimportant. In our two-dimensional network, it is readily seen that the lines parallel to AB are richer in atoms than those parallel to CE.

There is a particular distance between the lines in each line-grouping, the distance being characteristic of that grouping. Thus, the lines parallel to AB are separated by a distance AC, equal to the side of one of the small squares in the diagram; the lines parallel to CD are separated by a distance equal to half the diagonal of the same square, and so on. In a three-dimensional lattice there is similarly a characteristic spacing of the planes in each grouping of the atoms into planes.

Now the spacing of the planes or layers of atoms clearly depends on the kind of lattice we are considering. Conversely, if we can measure the distances between the layers, we can argue back to the kind of lattice. The problem of X-ray investigation of the structure of crystals is to measure the distances between the layers of atoms and to reason back from these measurements to the arrangement of atoms in the crystal.

The Braggs were amongst the earliest workers to inquire into the structure of crystals with the help of X-rays. The crystal actually consists of a lattice of atoms each of which diffracts the X-rays; the Braggs showed that this system is geometrically equivalent to a series of reflecting planes, the same planes as those we have just been considering. Each of these planes of atoms reflects the X-rays falling on it; so the crystal is rather like a pile of very thin glass plates, except that the distances between the atoms in the crystal are thinner than the thinnest of glass plates.

Consider, then, a beam of X-rays falling on the crystal, with its series of reflecting layers. In Fig. 48 CA is the beam of X-rays. Part of the ray CA is reflected at A in the top layer, and travels along AX; part penetrates to the second

layer and is reflected along BY; part penetrates still deeper. But consider only, for the moment, the rays reflected at A and B. The ray AX will be in advance of the ray BY, because it does not have to travel so far: to get to the points D and E, which are "level" with one another, the ray AX has to travel the distance AD, while the ray along BY has to travel the longer distance ABE.

Now each of the rays AX and BY is part of the original ray CA, so they start off in phase. As a rule they will be out of phase at D and E because the distances AD and ABE are not the same. But it may happen that the difference between AD and ABE is exactly equal to the wavelength of the light used. The crests of the ray AX will then coincide with those of the ray BY (but one wave further on), and we shall get a particularly bright reflection. If the ray AX happens to be half a wavelength in front of the ray BY, then the crests of one wave will coincide with the troughs of the other; the two rays will almost cancel one another out, and little reflected light will be seen.

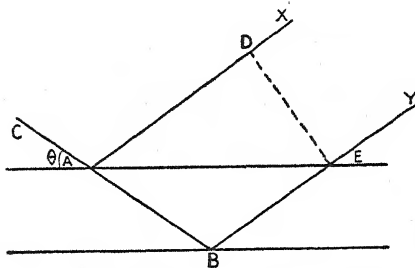


FIG. 48.—Reflection of X-rays from a crystal.

Actually, of course, we must consider more than two reflecting layers. If we take this into account, we see that when the rays AX and BY from the top two layers are in phase and reinforce one another, so do the rays from all the lower layers; so we get a very bright reflection. But when the rays AX and BY are out of phase, it does not follow that all the rays from the lower layers are out of phase too. Indeed this could not happen. What happens in this case is that the ray reflected from the third layer is in phase with AX, that from the fourth layer is in phase with BY, and so on alternately. The net result is that we get a weak, but not a very weak reflection.

It is, then, the very bright reflections which are of the greatest significance. To get a very bright reflection the angle θ and the wavelength of the light used must be just right; there is an equation connecting these two quantities with the distance between the reflecting layers.

[The difference in the distances the two waves have to travel is equal to $(AB + BE) - AD$, or $2AB - AD$ (Fig. 49).

Now

$$\frac{BF}{AB} = \sin \theta \quad \therefore AB = \frac{BF}{\sin \theta}$$

$$\frac{AF}{AB} = \cos \theta \quad \therefore AF = AB \cos \theta = \frac{BF \cos \theta}{\sin \theta}$$

$$\frac{AD}{AE} = \cos \theta \quad \therefore AD = AE \cos \theta = 2AF \cos \theta = \frac{2BF \cos^2 \theta}{\sin \theta}$$

Putting in these values,

$$\begin{aligned} 2AB - AD &= \frac{2BF}{\sin \theta} - \frac{2BF \cos^2 \theta}{\sin \theta} \\ &= \frac{2BF (1 - \cos^2 \theta)}{\sin \theta} \\ &= 2BF \sin \theta \end{aligned}$$

If the waves along AD and BE are to be in phase, this distance must be equal to λ , the wavelength of the light used. Writing d instead of BF (d being the distance between the reflecting layers)

$$\lambda = 2d \sin \theta]$$

What we want to find are the various possible values of d , the distance between the reflecting planes in the crystal. To do this we must know the wavelength of the light used and the values of the angle θ for which we get a particularly bright reflection. We can then use the equation connecting these quantities to calculate the value of d corresponding to each value of θ which gives a very bright reflection. Then, as we have seen already, we can argue back from all the possible values of d to the arrangement of the atoms and molecules in the crystal lattice.

The instrument used to obtain the values of θ for which

there is a maximum intensity of reflected light is the X-ray spectrometer. This instrument consists of the following essential parts :

(1) A source of X-rays. If possible, the X-rays should be all of the same wavelength (monochromatic) ; but usually two or three wavelengths will be present, besides a certain amount of " white " radiation (radiation of all wavelengths). If too many different wavelengths are present, each will give a very bright reflection at its own particular value of θ ; the consequent overlapping will make the results of little value.

(2) A system of slits to give a narrow beam of X-rays.

(3) A crystal-holder, and a mechanism to rotate it. The most convenient way of changing the value of θ so as to

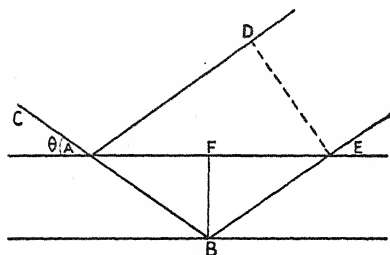


FIG 49.

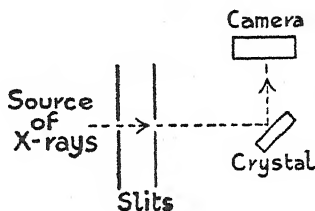


FIG. 50.—Arrangement of the parts in the X-ray spectrometer.

measure the brightness of the reflected light for different values of this angle, is by rotating the crystal ; the alternative is to rotate the beam of X-rays, but this is much less convenient.

(4) Photographic apparatus, to obtain photographic records of the brightness of the X-rays reflected from the crystal. An ionisation chamber can also be used for this purpose.

In point of time the Laue method preceded the Bragg method of investigating crystal structure ; in some ways the two are complementary.

When a crystal is being examined by the Laue method, a narrow beam of X-rays is focussed on to a thin section of the crystal ; the rays passing through this thin section are photographed. " White " X-rays are used, that is X-rays

of all wavelengths combined (just as visible white light consists of all the colours in the visible spectrum).

We must return to our idea of the crystal as a series of parallel planes, each of which can reflect X-rays. In Fig. 51 the dotted line is supposed to represent one of these reflecting planes. The ray AB which falls on it is reflected along the direction BC. Now, if the wavelength is just right, the rays reflected from the plane PQ will be in phase with those reflected from all planes parallel to PQ; a bright ray will emerge along the direction BC. But we are using white X-rays, so the right wavelength for this to happen will certainly be present.

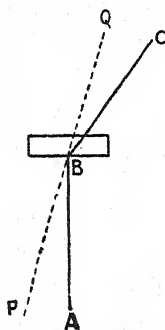


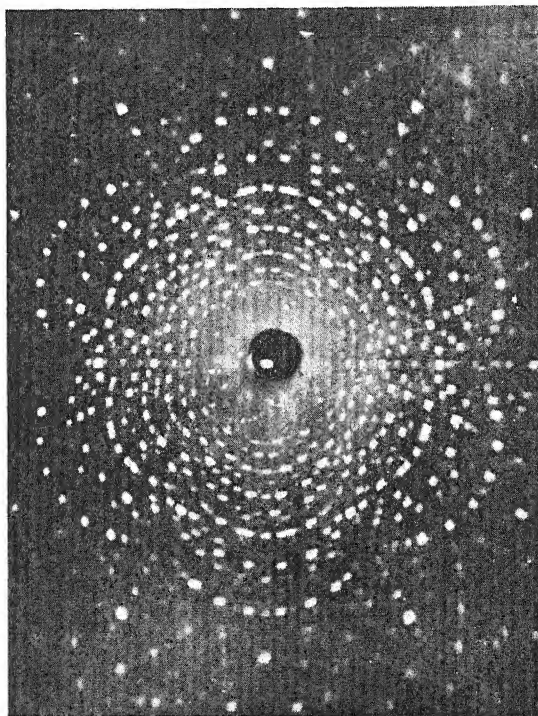
FIG. 51.—The principle of the Laue method.

Each other grouping of the atoms into planes will also give rise to a bright reflected ray; of course, these rays will all be in different directions. If a photographic plate is placed to receive the reflected rays, a bright spot will appear on the plate wherever one of these rays strikes it. The bright spots are arranged symmetrically over the photograph, as can easily be seen. From the positions of the spots we can argue back to the arrangement of atoms in the crystal that has produced them.

The Laue method has the advantage that a single photograph often enables us to elucidate completely the crystal lattice, whereas the Bragg method necessitates investigation of the crystal, face by face. On the other hand, the Laue method has the disadvantage that it does not give the absolute distances between the atoms, but only the relative distances; also the intensity of the bright spots in a Laue photograph is of little significance, whereas the intensity of the reflected light in the Bragg method gives useful information. In investigating a crystal from the point of view of structure, it is best to use a combination of both methods.

Both the Bragg and the Laue methods need fairly large and reasonably perfect crystals (although satisfactory investigations have been made on crystals less than a milli-

PLATE VII.



LAUE PHOTOGRAPH OF NEPHELINE.

(By kind permission of the "Mineralogical Magazine.")



metre across). Debye and Scherrer devised a means of applying the principle of the Bragg method to powdered crystals. This was a very valuable addition to the other methods, for many substances occur in minute crystals—often apparently amorphous—and can only be obtained with difficulty in large crystals.

The minute facets of the microcrystals in the powder are at all angles to the beam of X-rays which falls on them; some happen to be at the correct angles to reflect the light—just as in the application of the method to large crystals. We thus get a series of bright reflections—all those that are obtained in the ordinary Bragg method. Only now they are all obtained on a single photograph. The results are, therefore, more difficult to interpret, but not impossibly so.

The actual experimental arrangement is shown in Fig. 52. A strip of photographic film is fixed upright in a circle, and a small mass of the powder is placed at the centre. A

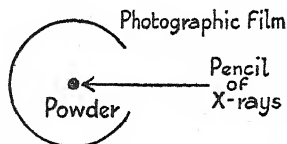


FIG. 52.—Arrangement of the parts in the powder spectrometer.

narrow pencil of X-rays is directed on to the mass, and is reflected in various directions by the crystals in the powder. The reflected light is received on the photographic film, where each direction of particularly intense reflection produces a bright line. The positions of these lines can be used to deduce the structure of the crystal, just as in the Bragg method.

It is a useful device to mix some sodium chloride with the powder. The sodium chloride gives lines in known positions in the photograph, and these lines can be used for comparison.

Having proved the utility of this method in the investigation of powders, Debye determined to apply the principle of the Bragg method to still smaller particles. He investigated the reflection of X-rays by gases. Here the light is reflected not from the faces of minute crystals, but from the individual molecules of the gas under examination; the molecules, like the minute crystals in a powder, are arranged

haphazard. Many important measurements of the arrangements of atoms in molecules have been made by this method ; some of them are dealt with at the end of the chapter.

In a gas or vapour the molecules are relatively far apart ; they do not have much distorting effect on one another. In a liquid, however, the distorting effect is considerable. Moreover, suppose we measure the distance between two chlorine atoms in liquid carbon tetrachloride. There is no means of knowing whether we are really dealing with two chlorine atoms in the same molecule, or whether they are in neighbouring molecules. The X-ray photographs of liquids are, therefore, difficult to interpret, and few useful results have been obtained in this way. The molecules in a liquid have neither the ordered array of crystalline structures, nor the independence from one another of gas molecules.

A remarkable development is the use of electrons in place of X-rays in this method of investigating gases. One of the most revolutionary ideas of wave mechanics is that massive particles (particles having mass) behave in some respects as if they were like waves. The relation between the wavelength of these waves and the mass of the particle with which they are associated is due to de Broglie ; it is :

$$\lambda = \frac{h}{mv}$$

(λ is the wavelength of the waves, h is Planck's constant, m is the mass of the particle, and v is its velocity.) Since we divide by the mass to obtain the wavelength, the wavelength is very small when the mass is large ; even the small masses that we measure in thousandths of grams are far too big to give a reasonably long wavelength. It is only when we come to particles like the electron that the wavelength becomes appreciable. (This is another of those cases in which the familiar ideas of mechanics break down when we come to deal with the small masses and high speeds of particles like the electron.)

The wavelength associated with cathode rays (high-speed electrons) has been measured ; it is, in practice, about one-twentieth of the wavelength of X-rays. On account of their

very short wavelengths, electron rays (cathode rays) have a much more intense interaction with molecules and a much greater effect on a photographic plate than have X-rays. This more intense interaction is of great importance. In the X-ray method of investigating gases and vapours an exposure of four or five hours is necessary; the electron rays are reflected by the gas molecules much more intensely than X-rays, and the reflected rays have a greater effect on the photographic plate, so that the exposure necessary is only a few tenths of a second. This reduces the practical difficulties considerably. But it does more than this. Many organic compounds decompose far below their boiling-points, so their vapours can be obtained only at great tenuity. To investigate such compounds by means of X-rays would entail impossibly long exposures, whereas they can be investigated quite conveniently by means of electron rays.

The electron ray method has been applied to solids as well as gases. On account of their more intense interaction with the molecules, they do not penetrate so far as do X-rays. They can, therefore, give more information about the surface layers.

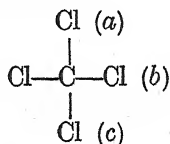
Measurements of interatomic distances made by the X-ray method agree with those made by the electron-ray method, so we can have considerable confidence in both methods.

The interatomic distances in the molecules of oxygen, nitrogen, bromine, etc.—these molecules all contain two atoms—have been measured by these methods. In the case of bromine, for instance, the measured distance between the atoms is 2.27 Å.U.; this compares very well with the value 2.26 Å.U. obtained spectroscopically. Another example is the measurement of the distance between the two oxygen atoms in carbon dioxide, CO_2 . The X-ray method gave the value 2.5 Å.U., and the electron-ray gave the value 2.25 Å.U. In the oxygen molecule the atoms are 1.21 Å.U. apart; so these results show quite clearly that the carbon atom in carbon dioxide has been interposed between the two oxygen atoms.

Interesting and valuable work has been done on the series of compounds :

Carbon tetrachloride	.	.	.	CCl_4
Chloroform	.	.	.	CHCl_3
Methylene chloride.	.	.	.	CH_2Cl_2
Methyl chloride	.	.	.	CH_3Cl

The distances between the pairs of chlorine atoms in the first three of these compounds have been observed and measured. In the CCl_4 molecule the distances are all the same : each chlorine atom is equidistant from every other chlorine atom. This shows that the molecule is tetrahedral ; if, for example, it were planar :



the distance between atoms (a) and (b) would be different from that between atoms (a) and (c), and both these distances would show themselves in the X-ray photograph.

Knowing the chlorine-chlorine distance and the tetrahedral shape of the CCl_4 molecule, it is a matter of simple geometry to calculate the carbon-chlorine distance. This distance turns out to be the same as the carbon-chlorine distance in the compound CH_3Cl , which can be measured directly by the X-ray and electron-ray methods. One might readily imagine that when the tiny hydrogen atoms are replaced by the much larger chlorine atoms, the carbon-chlorine links would be stretched to make room for them. But the stretching between CH_3Cl and CCl_4 is very small ; it appears, therefore, that the force to stretch a link is relatively large.

In CHCl_3 and CH_2Cl_2 the observed distances between the chlorine atoms are greater than in CCl_4 . Evidently the large size of the chlorine atoms is forcing the valencies apart at the expense of the hydrogen atoms. We can use the measured distances to calculate the angles between the carbon-chlorine links in the various compounds :



The values are :

CCl_4	.	.	$\theta = 109\frac{1}{2}^\circ$ (the tetrahedral angle)
CHCl_3	.	.	$116\frac{1}{2}^\circ$
CH_2Cl_2	.	.	124°

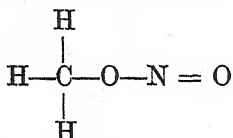
This table shows perfectly clearly the effect of the large chlorine atoms in forcing the links apart ; it is much easier to force the links apart than to stretch them.

These calculations could be confirmed if we could determine experimentally the carbon-hydrogen and chlorine-hydrogen distances. Unfortunately this is not possible : the hydrogen atoms do not interact intensely enough with X-rays and electron rays.

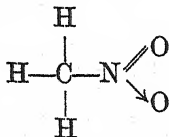
CHAPTER XV

STEREOCHEMISTRY : THE ARCHITECTURE OF MOLECULES

WE have already come across the idea of isomerism, that is, of substances whose molecules are composed of exactly the same atoms, but which are chemically different because the atoms are differently arranged in the molecules. Methyl nitrite and nitromethane, for example, are isomers ; the molecules consist of identically the same atoms built into two different structures. Methyl nitrite has the structure :



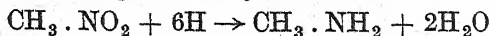
whereas nitromethane has the structure :



The important difference between these two compounds is that in the former an oxygen atom, and in the latter a nitrogen atom, is linked to the carbon atom. The difference in structure results in chemical differences between the two substances : they often react differently with the same reagent. When they are reduced, for example, methyl nitrite gives methyl alcohol and ammonia :



and nitromethane gives methylamine :

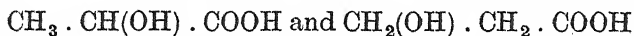


There are many similar cases of isomerism in which the isomers differ more or less considerably in chemical properties.

Lactic acid, which is formed when milk goes sour, raises an entirely new problem in isomerism. It has the formula $\text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \text{COOH}$. It exists in three forms, three isomers, but these are not isomers in the same sense as methyl nitrite and nitromethane; they are not chemical isomers. Two of the forms of lactic acid are identical in their chemical properties and in most of their physical properties. The third form is produced when equal amounts of the other two forms are mixed.

In spite of their similarity there is no doubt about the existence of the three forms of lactic acid. They are readily distinguished by their behaviour toward polarised light. One of the forms, the "dextro" form, rotates the plane of polarisation to the right. Another form, the "lævo" form, rotates it to the left. A half-and-half mixture of these two forms of lactic acid gives the third form, the "racemic" form. Racemic lactic acid has no effect on polarised light; the right-hand rotation caused by the dextro half is exactly undone by the left-hand rotation caused by the lævo half.

When we try to account for the existence of the dextro and lævo forms of lactic acid, it is no use supposing, say, that the hydroxyl group, OH, is attached to one carbon atom in one group, and to another carbon atom in another group. We should have in that case two such structures as :



But these would be two ordinary isomers which would differ chemically. And in any case the second compound is known; it is β -hydroxy-propionic acid, a substance quite distinct from the lactic acids. Any other such variation of structure would be equally useless as a means of accounting for the isomers of lactic acid. In seeking an explanation we have to consider, not merely which atom is linked to which, but the actual arrangement of the atoms in space, the way they are arranged about one another. This is the subject-matter of stereochemistry—the architecture of molecules, as it were.

Nowadays we have at least three physical methods of

investigating the ways in which molecules are built up : we have the measurement of dipole moments, the study of molecular spectra, and the X-ray methods of investigation ; all these give us information about the arrangement of the atoms in molecules. But the problem of lactic acid and similar compounds was solved by purely chemical means long before the modern physical methods were available.

In 1872 van't Hoff and Le Bel, independently, put forward the idea that the valencies of the carbon atom are directed toward the four corners of a tetrahedron. According to this

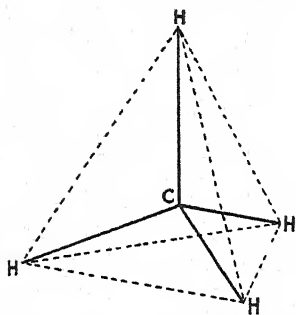
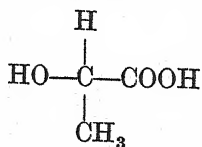


FIG. 53.—The methane molecule.

idea the atoms of methane, CH_4 , for example, are arranged as in the diagram ; the carbon atom is at the centre of the tetrahedron, and the four hydrogen atoms are at the corners. We shall see that there is ample evidence to support this view of "the tetrahedral carbon atom."

Now in place of the four hydrogen atoms of methane, there are four different groups attached to the central carbon

atom in lactic acid. The structure is :



These four groups are arranged at the corners of a tetrahedron, with the carbon atom at the centre. There are two ways, and two ways only, of arranging the four groups at the corners of a tetrahedron ; these are the ways shown in Fig. 54. These two arrangements are "mirror-images," as though each were the reflection of the other. If we seek for another arrangement we might, for example, interchange the CH_3 and COOH groups in the first arrangement ;

but it can readily be seen that this arrangement merely repeats the second arrangement, the one exactly fits the other. And so with any other changes of this kind; we always get either one arrangement or the other. But the two mirror-image arrangements do not fit. In the diagram the H and OH fit, but the CH_3 and COOH are the wrong way round. If we turn the first tetrahedron so that the CH_3 and COOH fit, then the H and OH will be the wrong way round. It is not possible to superimpose one mirror-image upon the other.

Van't Hoff and Le Bel suggested that these two arrange-

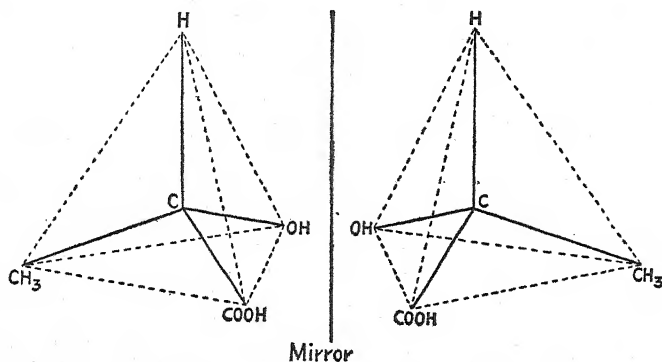
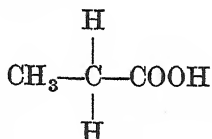


FIG. 54.—The dextro and laevo forms of lactic acid.

ments represent the dextro and laevo forms of lactic acid. The similarity between the two forms—the identity of the linkages and the relations between the atoms—is sufficient to account for the identity of the chemical properties of the two substances. The difference between the forms admits the possibility of certain physical differences such as the effect on polarised light. Indeed, it is just such physical differences that we ought to expect.

In lactic acid the mirror-image (enantiomorphous) forms are not identical. We can, of course, construct the mirror-image of any compound—merely by placing a diagram or model of the molecule before a mirror. But the mirror-image will often turn out to be identical with the structure

with which we started. We may take propionic acid as an example. Its structure is :



We have here a compound which is derived from lactic acid by putting a hydrogen atom in place of an OH group. There are only three different groups, not four, round the central carbon atom. If we draw the mirror-image of this

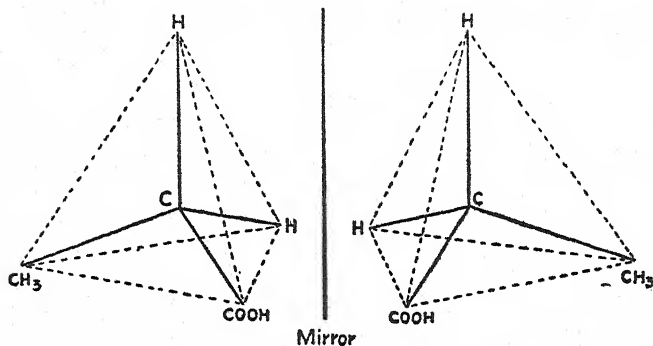


FIG. 55.—The propionic acid molecule.

molecule we find that it is identical with the original structure, that is, it can be superimposed upon it. If, for example, we twist the CH_3 and COOH groups of the second form round so as to fit over the corresponding group in the first form, then the lower H in the second form becomes the apex of the tetrahedron and the two H's fit. Thus we should not expect propionic acid to show any optical activity, that is, to have any effect on polarised light. This is actually the case.

The two forms of lactic acid, dextro and lævo, have exactly the same chemical properties. When the acid is prepared by chemical means it is always the half-and-half racemic mixture that is obtained. How then is it possible to get either form separate from the other? Well, for one

thing lactic acid often occurs in nature in one form or the other, either completely dextro or completely lævo ; nature has already carried out the separation for us. It is indeed a remarkable fact that whenever a compound can exist in optically active forms, it nearly always does exist in one or other of these forms in nature ; whereas the product made in the laboratory is optically inactive. There is as yet no complete explanation of why natural products are optically active.

But suppose we have prepared a racemic mixture in the laboratory. Is it possible to separate this into dextro and lævo forms ? Is it possible to resolve it, as chemists say ?

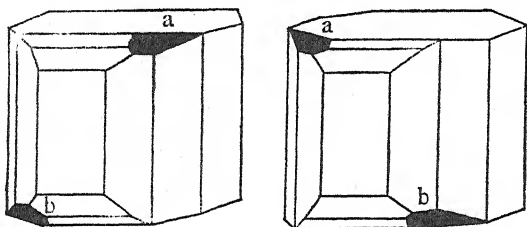


FIG. 56.—Mirror-image crystals of sodium ammonium *d*-tartrate and *l*-tartrate. From Bernthsen's *Text-book of Organic Chemistry* (by permission of Messrs. Blackie).

It is ; there are at least three ways in which a racemic mixture may be resolved.

(1) In some cases and under certain conditions the two forms crystallise into separate crystals, and the two kinds of crystals may be sorted out by hand. The crystals, like the molecules themselves, are mirror-images of each other ; the two kinds of crystals can be distinguished from each other by some of the crystal facets. As can be imagined, the sorting out is not too easy a process. It is not a matter for surprise, by the way, that the crystals should be mirror-images. The molecules in crystals are regularly arranged ; so that as the molecules are mirror-image forms it sometimes happens that the crystals themselves are mirror-image forms too.

(2) It is often possible to find another optically active compound which reacts with the compound we wish to

resolve. Strychnine, for instance, reacts with lactic acid to give strychnine lactate. Now strychnine occurs in nature in the *lævo* form. And so when this natural product reacts with racemic lactic acid prepared in the laboratory we get the two components :

lævo-strychnine dextro-lactate
lævo-strychnine *lævo*-lactate

These two compounds are not mirror-image forms ; the mirror image of the *lævo*-dextro compound is the dextro-*lævo* compound and not the *lævo*-*lævo* compound. Thus

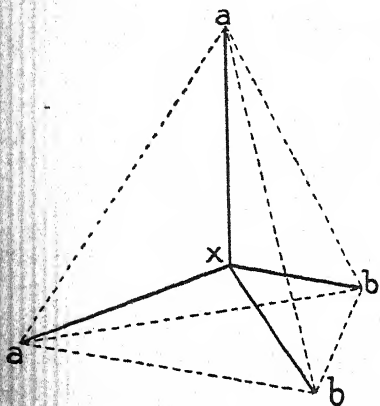


FIG. 57.

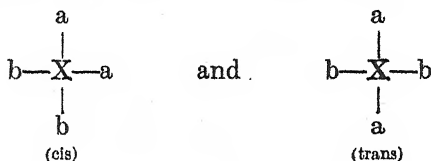
we have two forms of strychnine lactate which are not optical, but chemical, isomers. They differ in such properties as solubility, and therefore they can be separated. If we then remove the strychnine we shall be left with pure dextro lactic acid in the one case and pure *lævo* lactic acid in the other.

(3) It sometimes happens that the two forms of an optically active compound react at different rates with another optically active compound. Pasteur separated out the *lævo* form of tartaric acid from a racemic mixture by using a certain mould (which probably contained optically active material) to destroy the dextro form in the mixture ; the *lævo* compound was not affected by the mould.

The whole subject of optically active substances is evidence in favour of the tetrahedral theory of the carbon atom. But it is desirable to have the theory confirmed by other evidence. Measurements of dipole moments, and other modern methods, lend support to the tetrahedral theory, and there is in addition further chemical evidence.

Consider a molecule, Xa_2b_2 , where *a* and *b* stand for atoms

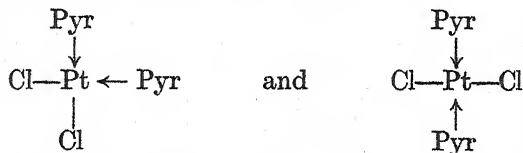
or groups linked to a central X atom. Such a compound might be either planar or tetrahedral. If it is tetrahedral its structure is like that shown in Fig. 57. Any rearrangement of the a's and b's simply repeats the original form; so there is only one compound. If, however, the compound is planar, it can have either of the structures:



These are obviously not mirror images of one another, and therefore they are not optical isomers. They are, in fact, cis-trans isomers, chemical isomers with chemically distinct properties.

Thus we can distinguish between the tetrahedral and the planar arrangements by seeing whether a compound of the type Xa_2b_2 exists in one or in two forms. In the case of carbon it is found that all such compounds as dichloromethane, CH_2Cl_2 , dibromomethane, CH_2Br_2 , dichloropropane, $CH_2(CH_2Cl)_2$, etc., exist in one form only. The conclusion is that the arrangement of groups around the carbon atom is tetrahedral.

The carbon atom is always tetrahedral; it never gives a planar arrangement. Indeed, this is true of most atoms when they are attached to four groups. But certain platinum compounds are planar. For instance, the formula $Pt(Pyr)_2Cl_2$ stands for the two compounds:



("Pyr" stands for the compound pyridine. Pyridine contains a nitrogen atom which is capable of forming a coordinate link with the platinum atom.) If the two structures were tetrahedral in form they would be identical—they would represent one and the same substance. But there

are actually two chemically distinct substances; this is evidence of a planar structure.

We have thus a chemical means of distinguishing between tetrahedral and planar arrangements in molecules; there are other distinctions as well. In general, we find that the tetrahedral is the more common arrangement; it often persists even when there are fewer than four groups attached to the central atom.

This is the case with the ammonia molecule, NH_3 , in which there are *three* hydrogen atoms attached to the nitrogen molecule; the structure is shown in the diagram. Incidentally, it is very probable that the nitrogen atom is

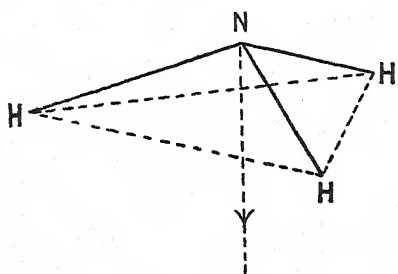


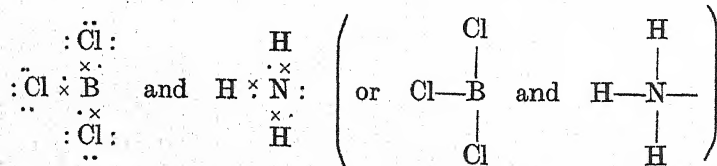
FIG. 58.—The ammonia molecule. The arrow indicates how the nitrogen atom oscillates.

oscillating at right angles to the plane containing the three hydrogen atoms, so that it moves from one side of the plane to the other.

The carbonate ion, CO_3^{--} , is of the same type as ammonia, the type ab_3 . But though there is an apparent similarity, the structure of the carbonate ion is quite different from

that of the ammonia molecule. Determinations of the crystal structures of carbonates show that the arrangement of the atoms in this ion is planar.

Boron trichloride, BCl_3 , is another case in which the arrangement is probably planar. Now if you compare this molecule with the ammonia molecule we have the structures :



There is the important difference that the nitrogen atom has a lone pair, whereas the boron atom has not. In the

planar arrangement of boron trichloride the three links are as far apart as they possibly can be : at angles of 120° . It is as though they were repelling each other. In the ammonia molecule we must count the lone pair of the nitrogen atom along with the three covalent links. After all, it is a pair of electrons just as much as they are. Now if the lone pair, as well as the three covalent links, all repel one another, then they will give a tetrahedral arrangement ; for in this position they are as far apart as they possibly can be. As we have said, this is the actual arrangement in the ammonia molecule. It is, indeed, almost generally true that when an atom has an octet of electrons, then its valencies are arranged tetrahedrally.

There is good chemical evidence for the tetrahedral

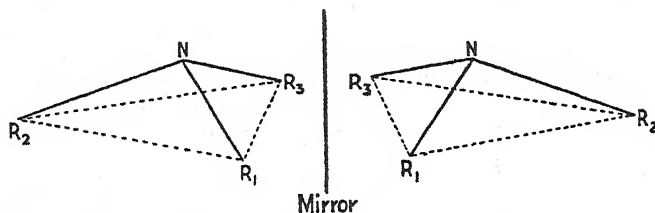


FIG. 59.

arrangement of groups about a nitrogen atom. Consider a derivative of ammonia—a compound of the form $NR_1R_2R_3$, that is, with three different groups replacing the three hydrogen atoms. (Such a compound is called an amine.) If a molecule of an amine is tetrahedral it is clearly not identical with its mirror-image ; there are two mirror-image forms. The molecule should, therefore, be optically active. But this is not the case ; amines cannot be resolved into two optically active forms. Probably this is because the nitrogen atom oscillates in the way already suggested. Oscillation of this kind would quickly reduce an optically active form to a racemic mixture, because the transference of the nitrogen atom from one side to the other, by oscillation, changes one form into the other.

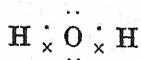
But if we can stop the oscillation of the nitrogen atom we should expect to get a compound that can be resolved.

Now the lone pair of electrons on the nitrogen atom can form a co-ordinate link with oxygen, as it does in the amine oxides. This stops the oscillations of the nitrogen atoms, and the compound can be resolved. This chain of argument and the experimental verification are evidence in support of the tetrahedral arrangement of the nitrogen valencies; they are also evidence in support of the oscillation of the nitrogen atom through the plane of the attached groups in the amines.

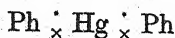
And now consider the case of a sulphur atom united to three different groups. This case is quite different from the case of the amines: the sulphur atom does not oscillate as the nitrogen atom appears to do. There is no reason, therefore, why the mirror-image forms should racemise at once. A molecule of this kind—containing a sulphur atom attached to three different atoms or groups—can be resolved into optical isomers, even though there is no atom or group occupying the fourth apex of the tetrahedron.

Even when there are only two atoms or groups linked to a central atom—as, for instance, in the water molecule, H—O—H —even in such cases a linear arrangement is rare. Instead of the two links being in a straight line they are at an angle of about 110° , that is, they are at about the same angle as two of the arms from the centre of a tetrahedron to the apexes. It is as though this were the beginning of a complete tetrahedral molecule.

There are compounds in which two valencies lie in a straight line. To find such compounds we must get away from molecules like water, for there the central atom has a complete octet:



As we have seen, an octet of electrons usually means that the valencies will be arranged tetrahedrally. In mercury diphenyl, however, the mercury has only four valency electrons:

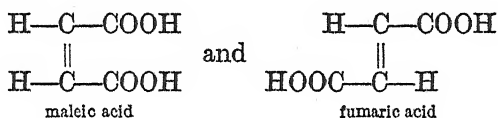


(Ph is the symbol for the phenyl group, which, like hydro-

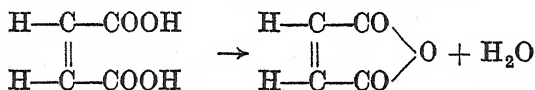
gen, can supply one electron to a link.) Here the two valencies arrange themselves in a straight line, so the compound is linear.

Besides the optical isomerism which we have been considering, there is another kind of isomerism; this kind as well cannot be explained merely by finding which atom is attached to which. Isomers of this sort are known as geometrical isomers; to explain their existence we must consider the architecture of the molecules again.

Maleic and fumaric acids are geometrical isomers; they have each a double bond between two carbon atoms. The structures are:



The two forms are clearly not mirror-images of each other; they are, therefore, chemical isomers and not optical isomers. The following example illustrates the chemical differences; it illustrates also how chemical differences may arise out of differences in structure. Maleic acid forms an anhydride:



by the loss of a water molecule, much more readily than fumaric acid does. The reason is obvious from the structure: the two OH groups in maleic acid are conveniently situated to react together and give a water molecule. In order that the OH groups in fumaric acid should react similarly, rotation about the double bond is necessary; fumaric acid must first be changed to maleic acid before it will give an anhydride. It turns out that fumaric acid gives an anhydride with difficulty, and then it is the same anhydride as that given by maleic acid. This shows that rotation about the double bond is very restricted—a single half-turn about the double link would convert one isomer into the other, but this conversion is difficult to accomplish.

This is just what we should expect from the tetrahedral

model of the carbon atom. In forming a single link, two tetrahedra are held together corner to corner, so there is no reason why they should not swivel round about the link. But in forming a double link, the tetrahedra are held edge to edge; it is impossible to rotate one tetrahedron round the other and keep the edges touching all the time. Similarly, in forming a triple link, the two tetrahedra are connected face to face.

It might readily be thought that a double bond would be stronger than a single bond, and that a triple bond would be stronger still. As a matter of fact it does take more energy to break a double link than a single link, and more still to break a triple link. But a double link is always a weak

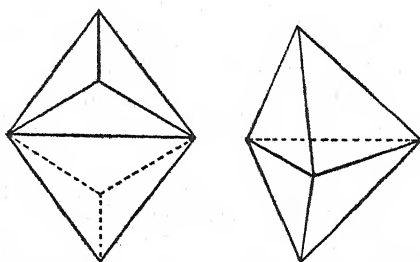
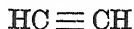


FIG. 60.—*Left* : The double link. *Right* : The triple link.

point in a molecule, and a triple link even more so. This is because it is relatively easy to break one of the links in a double link, and so leave only a single link. In a triple link it is easy to break two links and leave only one again. The normal angle between two carbon links is the tetrahedral angle, 110° . In the double bond the links are strained from the normal angle to directions that are almost parallel; the angle between the links is reduced to the neighbourhood of 0° . The state of strain in the double link accounts for its weakness. There is still more strain in a triple link.

The nitrogen atom shows an extraordinary contrast to carbon—the reason for the difference is a problem still to be solved. In nitrogen the double bond is more stable than the single, and the triple bond is more stable still. The nitrogen molecule contains a triple bond: $\text{N} \equiv \text{N}$. The

bond is so stable that uncombined nitrogen is remarkably inert ; it is extremely difficult to get it to react with other substances. Acetylene, with the similar structure :



but with the triple bond between carbon atoms, is so ready to react that it can even be exploded.

The allene derivatives contain a special system of double

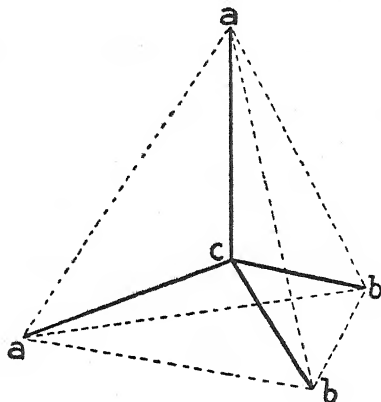
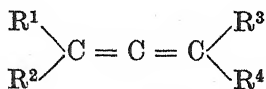


FIG. 61.

links between carbon atoms. The general formula of these compounds is :



The signs R^1 , R^2 , etc., stand for groups attached to the carbon atoms. Now, referring again to the diagram of the tetrahedral carbon atom, it will be seen that the planes aCa and bCb are at right angles to each other. The two links Ca may form a double bond connecting the central carbon atom to some other atom (along the side aa). Similarly, the two links Cb may form a double bond uniting the carbon atom to another atom along the side bb . If the theory of the tetrahedral carbon atom is correct these two double bonds should be at right angles to each other.

collide with one another, and when they collide they exchange some of their energy. There is no increase or decrease in the total energy during a collision; one molecule gains exactly what the other loses; but if we consider one particular molecule, its energy is continually changing owing to collisions.

The number of molecules in the amounts of gas with which we are usually concerned is extremely large; at 0°C and 1 atmos. pressure a cubic centimetre of gas contains about 3×10^{19} molecules. (Even in the best vacuum we can get, there are still some ten million odd molecules to the cubic centimetre.) As the number of molecules in question is so immense we are justified in applying statistical methods

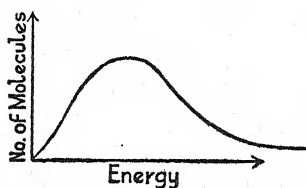


FIG. 64.—Distribution of energy amongst the molecules in a gas.

to the investigation of the properties of a gas. Suppose, for instance, we are considering the energy of the molecules. A certain value of the energy will be the most probable. There will be more molecules with this amount of energy than with any other amount; we can calculate just what proportion of

the molecules have this most probable amount of energy. We can calculate also what proportion of the molecules have half this amount of energy, what proportion have double, and so on. The results are shown in the graph, where the possible values of the energy are plotted against the proportion of molecules with that energy.

There can be no reaction between molecules unless they collide with one another. The speed of a reaction will thus depend, amongst other things, on the frequency with which molecules collide. We can calculate the "collision number" from the kinetic theory; the collision number is the number of collisions per cubic centimetre per second in the gas.

From the measured rate of reaction we can calculate how many molecules actually react; we find that it is usually many less than the number of molecules colliding. Evidently it is usually only a small proportion, perhaps a millionth, of

the total number of collisions which leads to reaction. There must be some other condition besides collision which must be satisfied before two molecules will react. This condition might depend on the energy of the colliding molecules, on their direction of approach, on the presence of a third molecule at the moment of collision, etc.

Actually we can get quite a long way by supposing that the only condition to be satisfied is that the colliding molecules must have a certain minimum amount of energy. If they have less than this amount of energy, they will not react. This minimum amount of energy is called the energy of activation of the reaction.

The kinetic theory tells us how the energies are distributed amongst the molecules; how many molecules, for instance, have an energy greater than a certain specified value. Thus, in a collision involving two molecules, we can find the chance that the *total* energy of the two molecules is greater than the energy of activation, that is, the chance of a collision leading to chemical reaction. [If E is the energy of activation, a fraction $e^{-E/RT}$ of the collisions lead to reaction. Here e is the exponential function, 2.718, R is the gas constant, and T is the absolute temperature.]

The necessity for activation before reaction can take place accounts for the great diversity in the speeds of reactions. Some reactions take years or perhaps centuries, whereas others—explosions—are over in a fraction of a second. In some reactions the energy of activation is extremely small, almost zero, so that every collision is effective; the reactions between the vapours of the alkali metals and the halogens are of this nature. To investigate a reaction of this sort it is necessary to use very low pressures (*e.g.* 10^{-3} mm.). This cuts down the actual number of collisions, and so prevents the reaction taking place at an unmanageably fast rate. When, on the other hand, the energy of activation is very high, it is only very rarely that molecules collide with enough energy to react, so the reaction occurs very slowly. [The great variety in the speeds of reactions is due largely to the exponential nature of the factor $e^{-E/RT}$.]

The speed of a chemical reaction usually increases con-

siderably when the temperature is raised; the speed may quite well be doubled for a 10°C rise. When the temperature of a gas is raised the molecules move about more vigorously. This leads to an increase in the collision number, and hence to an increase in the rate of the reaction; but this is altogether insufficient to account for the observed increase in the rate. The increase in the energy of the molecules has another effect: not only are there more collisions per second, but in a much greater proportion of these collisions there is sufficient energy to lead to reaction.

In the diagram the continuous line OBD indicates the distribution of energy amongst the molecules in a mass of gas at a low temperature; most of them have a small amount of energy, and only a few have a large amount. The energy of activation is represented by OA. Those which have an

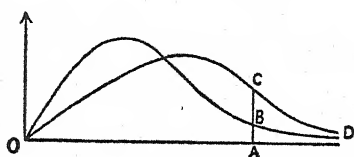


FIG. 65.

amount of energy greater than OA, are able to react; the number capable of reacting is given by the area ABD. When the temperature is raised, the average energy of the molecules is increased; there are now fewer molecules with a small amount of energy and many more with a large amount. The number of molecules capable of reacting, that is, with energy greater than OA, is given by the area ACD. This area is much greater than ABD, so that many more molecules will react even when the rise in temperature is but slight.

[The velocity constant, k , of the reaction is given by $Ce^{-E/RT}$, where C is very nearly constant. Taking logarithms we get

$$\log_e k = \log_e C - \frac{E}{RT}$$

Differentiating,

$$\frac{d \log_e k}{dT} = \frac{E}{RT^2}$$

To take an example, suppose that $E = 30,000$ cal. and $T. =$

500° Abs. Then for a 10° rise in temperature, the change in $\log_e k$ is

$$10 \times \frac{30,000}{2 \times 500^2} = 0.6$$

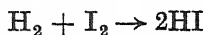
So the reaction goes $(2.718)^{0.6} =$ nearly twice as fast.]

A check on this theory is provided by a double calculation of the energy of activation from measured values of the reaction velocity :

(1) We know the collision number, and from the observed rate of reaction we can find what fraction of these collisions is effective in producing reaction. This fraction enables us to calculate the energy of activation. [The fraction is actually equal to $e^{-E/RT}$.]

(2) We can also measure the rate at which the reaction velocity increases with increase of temperature ; this rate is called the temperature coefficient of the reaction. This gives us another value for the energy of activation ; if we look again at Fig. 65 we see that the increase in area between ABD and ACD depends on where we draw the line ABC. [E is actually calculated with the aid of the relation $\log_e k = \log_e C - \frac{E}{RT}$. $\log_e k$ is plotted against $1/T$ so that a straight line is obtained ; the slope of this line is E/R , and R , the gas constant, is known.]

The theory we have just been considering applies primarily to bimolecular reactions, that is, to reactions involving two molecules. The reaction between hydrogen and iodine to give hydrogen iodide :



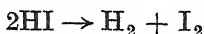
is a reaction of this sort. Now the rate of this reaction is proportional to the number of collisions between hydrogen and iodine molecules, and hence to the concentrations of both these gases. This means that if we double the concentration of either the hydrogen or the iodine the reaction will go at double the speed. We can express the result concisely by writing :

$$\text{Speed of reaction} = k[\text{H}_2][\text{I}_2]$$

where $[\text{H}_2]$ is the concentration of hydrogen and $[\text{I}_2]$ that of

iodine. k is a constant called the velocity constant of the reaction.

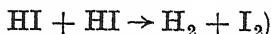
In some bimolecular reactions both reacting molecules are alike. An example is found in the decomposition of hydrogen iodide :



which is the reverse of the reaction just discussed. The rate of this reaction is proportional to the number of collisions between pairs of hydrogen iodide molecules, and hence to the square of the concentration of hydrogen iodide :

$$\text{Speed of reaction} = k'[\text{HI}]^2$$

Thus, if we double the concentration of hydrogen iodide, the reaction will take place *four* times as rapidly. (Perhaps the reason for the introduction of the square of the hydrogen iodide concentration is made clearer if we write the reaction :

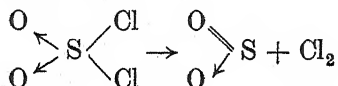


Often the rate of decomposition of a substance occurs at a rate proportional simply to the concentration, and not to the square of the concentration. The natural way to explain this is to suppose that each molecule of the substance decomposes on its own, independently of the other molecules. An almost perfect example of a reaction of this kind is found in the disintegration of a radioactive element like radium ; each atom of radium breaks up by itself, without reference to what the other atoms of radium are doing.

Reactions of this kind are called unimolecular reactions. When we try and apply the idea of energy of activation to such reactions we get into difficulties. At first sight it seems quite easy ; we have only to suppose that a molecule decomposes whenever it acquires the necessary energy of activation, and we can account for the rate and temperature coefficient of the reaction. Suppose, however, we decrease the concentration of the reacting gas until it is very low. Eventually the molecules will be so far apart that they will not collide with one another at all. This means that the energy of each individual molecule is fixed, it is no longer continually changing, as it is under ordinary conditions. A certain fraction of the molecules have energies in excess of

the energy of activation, and these molecules can react. But when these few molecules have decomposed, the reaction will stop ; the other molecules have no means of acquiring the energy of activation necessary for reaction.

Thus it appears that unimolecular reactions must depend on collisions after all. But why then are they not bimolecular ? The explanation of this paradox was suggested by Lindemann : he supposed simply that a short time elapses between the activation of a molecule and its decomposition. This assumption is quite reasonable, for it may be necessary for the energy to rearrange itself in the molecule, during the time between activation and decomposition. For instance, sulphuryl chloride decomposes according to the equation :



We can imagine that, during the decomposition, the vibrations in and out of the links between the sulphur and the chlorine atoms become more and more violent until eventually they break. It may take an appreciable time for the energy of activation of the molecule to get into these links and so set them vibrating.

Let us see how this idea works out. When the gas is concentrated, molecular collisions are frequent, so that an activated molecule is much more likely to lose its energy of activation in a collision than to decompose ; the average time that must elapse between activation and reaction is much longer than the average time between collisions. Thus we can say that not every molecule will react after activation, but only a certain small proportion of them ; most of the molecules that become activated are deactivated by collision instead. Now molecular collisions are frequent, so the supply of activated molecules is readily maintained, and there is always the same fraction of the molecules in the activated condition. There is a slow drift amongst the activated molecules toward decomposition, but this has an inconsiderable effect on the fraction of molecules activated.

The rate of the reaction is proportional to the concentration of molecules activated, and this in turn is proportional to the total concentration of the reacting gas ; hence the rate of the reaction is proportional to this total concentration.

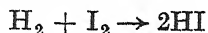
But now suppose the concentration of the gas is greatly decreased. The molecules collide much less often, so that a molecule which has become activated is much more likely to react than to collide. The supply of activated molecules can no longer be maintained by collisions, so we *shall* get the falling-off in the reaction velocity already predicted. The reaction should now be bimolecular, for decomposition occurs after *every* collision leading to activation instead of after only a small proportion of such collisions. Two activated molecules collide and then react, just as in an ordinary bimolecular reaction.

According to this theory, unimolecular gas reactions should behave like bimolecular reactions when they take place at low pressure (*i.e.*, low concentration). This prediction has been verified for nearly all known unimolecular reactions ; the rate is proportional to the concentration over quite a large range of pressures, but at low pressures it becomes proportional to the square of the concentration. As we have seen, this is due to the small number of collisions in the gas at low pressure. Suppose we keep the pressure of the reacting gas low, but add another gas to it, this other gas acting merely as a diluent. The number of collisions in the gas mixture will now be quite large again, so that the supply of activated molecules is maintained ; the reaction will thus remain unimolecular, even though the pressure of the reacting gas is low.

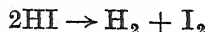
An interesting point is that hydrogen is found to be much more effective than other gases in maintaining the supply of activated molecules. This is partly because hydrogen molecules, with their small mass, move much more rapidly than molecules of other gases ; so they collide much more frequently with other molecules.

Just as reactions ordinarily unimolecular become bimolecular at low pressures, so do some reactions which are bimolecular at ordinary pressures become unimolecular at

high pressures. The distinction between uni- and bimolecular reactions is much less sharp than was previously imagined. Of course, a reaction like :

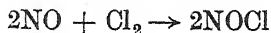


must remain bimolecular under all conditions, since it always depends directly on collisions between two molecules. On the other hand, a reaction like :



where there is only one reacting substance, might become unimolecular at high pressures ; that is to say, the hydrogen iodide molecules might decompose on their own, not only on collision with other hydrogen iodide molecules. As a matter of fact, such behaviour has never been observed in this particular reaction, but bimolecular reactions which become unimolecular at high pressures do exist.

There is a possibility of the existence of reactions involving collisions of more than two molecules. Reactions involving the collision of three molecules are called termolecular reactions. Such reactions are rare—indeed, there is no case of a termolecular reaction established beyond doubt—for collisions involving three molecules are much rarer than collisions involving two molecules. It is quite likely that such reactions as the combination of nitric oxide and chlorine :



are termolecular.

CHAPTER XVII

PHOTOCHEMISTRY

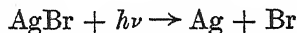
A GREAT many chemical reactions take place under the action of light, which supplies the energy necessary to set the reaction going. The energy of the light exists, as we know, in minute packets called quanta; molecules are able to absorb light-energy a quantum at a time, and so become activated. It is important to note that we never get the absorption of a fraction of a quantum; either a whole quantum is absorbed, or none.

It is generally visible and ultra-violet light that are photochemically active; infra-red light has but little effect on chemical reactions. The two former kinds of light have the effect of raising the molecule to a higher electronic energy level, rather than of making it vibrate or rotate more rapidly. There is, therefore, an essential difference between this kind of activation and that produced by collisions between molecules—indeed, the term “excitation” is often used to describe the former process, so as to emphasise this difference. Activation by collision has the effect of making the vibrations of the molecule more violent and so has a direct effect in making the molecule less stable, or, what comes to the same thing, more ready to react. When, however, a molecule absorbs a quantum of light-energy, its vibrations are not *directly* affected, so the energy absorbed may not be *immediately* available for chemical reaction.

It may happen that a molecule is excited by the absorption of light, but does not react chemically. It is obviously of interest to know what fraction of the excited molecules do react. The “quantum yield” of a reaction is a measure of this fraction; it is the ratio of the number of quanta of light absorbed by the reacting substance, to the number of molecules which actually react.

The quantum yield of a reaction can be measured experimentally; we can measure how much of the reactant is used up, and we can measure how much light is absorbed during the reaction. The quantum yield, therefore, can be used to give us information about the mechanism of the reaction.

Each quantum of light absorbed excites one molecule. If it so happens that every excited molecule reacts chemically, then it follows that the quantum yield will be unity (provided, of course, that none of the unexcited molecules react). A reaction for which this is true is the decomposition of silver bromide, giving metallic silver and bromine :



(Ag is the symbol for silver, and $h\nu$ represents the quantum of light absorbed.)

This reaction, the "photodecomposition" of silver bromide, is the essential reaction of photography. A photographic plate consists of a large number of very small grains of silver bromide suspended in gelatin. Although the grains are so small, yet they each contain a large number of AgBr molecules. The stages in taking a photograph are :

(1) The plate is exposed to light from the object to be photographed. Some of the silver bromide is decomposed by the light, giving metallic silver and free bromine. The bromine is taken up by the gelatin, so there is no chance of its recombining with the silver, and forming silver bromide once more.

(2) The plate is developed. A certain number of the grains of silver bromide in the exposed plate contain free atoms of silver. During the development process, the whole of the bromide in these grains is decomposed, setting free metallic silver; while those grains which have not been affected by light, and contain no free silver, are not affected by the development process.

Developers are mild reducing agents, such as pyrogallol. They can set free metallic silver from silver bromide, themselves taking up the bromine. But they can only do this if there is a little metallic silver present to begin with. Thus

it is only those grains containing a few atoms of silver—produced by the action of light—that are developed in this process. There must be enough silver atoms to form the beginnings of a crystal of silver.

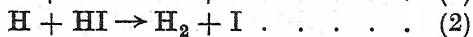
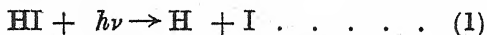
The development process really serves to augment the effect produced by light. Only a few silver bromide molecules are decomposed by light in the first place; during development a whole grain of silver bromide is converted into metallic silver, for every few atoms of silver set free on illumination.

(3) The plate is fixed. During this process any unchanged grains of silver bromide are dissolved out of the plate; sodium thiosulphate solution may be used for this purpose. The purpose of this process is to enable the plate to be safely exposed to light again; there is no longer any silver bromide present that might be decomposed by light.

(4) The “negative” obtained in this way is used to print the “positive.”

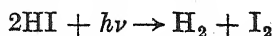
However, to return to our main theme. In 1913, Einstein proposed as a general law that the quantum yield of a reaction is always unity. This has been called the law of photochemical equivalence. It does hold accurately in certain cases, such as the reaction just considered; but quantum yields differing from unity are of very frequent occurrence.

A quantum yield of two is often met with, as, for example, in the photochemical decomposition of hydrogen iodide. The value of two arises in the following way: The action of the absorbed light-quantum is to dissociate the molecule of hydrogen iodide; on dissociation an atom of hydrogen and an atom of iodine are produced (1). The hydrogen atom produced reacts with another molecule of hydrogen iodide, giving another atom of iodine (2). And finally the two atoms of iodine combine together (3).

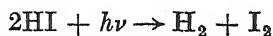


(In the first of these reactions, $h\nu$ represents the quantum

of light absorbed.) This series of processes is equivalent to :



so that two molecules of hydrogen iodide decompose for each quantum absorbed. (It is to be understood that the equation :

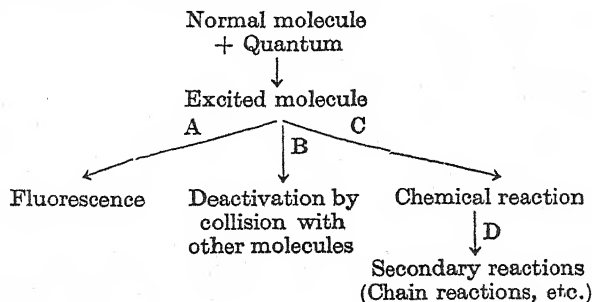


does not represent a single process ; it is the result of three separate processes.)

The quantum yield may rise above unity for other reasons than those just described. Sometimes the molecule originally excited is simply the first link in a long chain of processes which travels right through the mass of the reacting substances. Reactions of this sort are known as chain reactions ; they are dealt with more fully in the next chapter.

On the other hand, there are reactions with a quantum yield of less than unity. It is evident in these cases that not all the absorbed light-energy is effective in causing reaction ; something else is happening to some of it. Sometimes part of the energy is radiated away again, so that the substance fluoresces. Sometimes, too, part of the energy is lost in collisions with other molecules. In both cases some of the absorbed quanta are "wasted" as far as chemical reaction is concerned, and the quantum yield is less than unity (or less than two, if the reaction is one like the hydrogen iodide reaction, whose quantum yield is normally two).

We can summarise all the various things that can happen to an excited molecule in the scheme :



The quantum yield will be unity only when C occurs to the practical exclusion of A, B, and D. A and B are factors tending to lower the quantum yield below unity ; D tends to increase it above unity.

The energy of the quantum is $h\nu$, the frequency of the light multiplied by Planck's constant. Thus the higher the frequency of the light (the bigger the value of ν), the larger the size of the quantum. We should, therefore, expect that light of high frequency would be more active chemically than light of low frequency. This is borne out by experiment : blue light, which is towards the high-frequency end of the spectrum, is more active than red light, which is at the low-frequency end, and ultra-violet light is still more active than blue light.

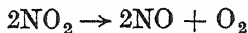
As we go from the red end of the spectrum to the violet end, the energy in the light-quanta steadily increases. Now, to decompose a compound usually requires a perfectly definite amount of energy ; so it may arise that violet light but not red light is able to bring about the decomposition. Somewhere between the red and the violet there is a point where the light-quanta are just, but only just, big enough to decompose the compound ; if we move a little from this point towards the red end of the spectrum, the quanta will be just too small, and the compound will not be decomposed.

Thus there is a particular light-frequency such that higher frequencies cause reaction to occur, whilst lower frequencies do not. The point where reaction can just, but only just, take place, is called the photochemical threshold of the reaction.

It is often by no means easy to observe this photochemical threshold. The main reason for this is that substances do not absorb all kinds of light equally well ; we often meet with substances that absorb, say, blue light but not red light, or green light but not violet light. So that if we try to follow the effect of different light-frequencies on a reaction we are in many cases brought to a halt because the reactants cease to absorb at some point in the spectrum. If the threshold frequency falls in a region of the spectrum which

is not absorbed by the reactants, it will be very difficult to find out exactly where it does lie.

A reaction which shows a photochemical threshold quite clearly is the decomposition of nitrogen peroxide, NO_2 ; nitric oxide and oxygen are produced :



It is found that with wavelengths longer than 4360 Å.U. no reaction takes place at all; the quanta of light have not sufficient energy to set the molecules of NO_2 vibrating so violently that they dissociate. The quantum yield in this region of long wavelengths—long wavelengths correspond to

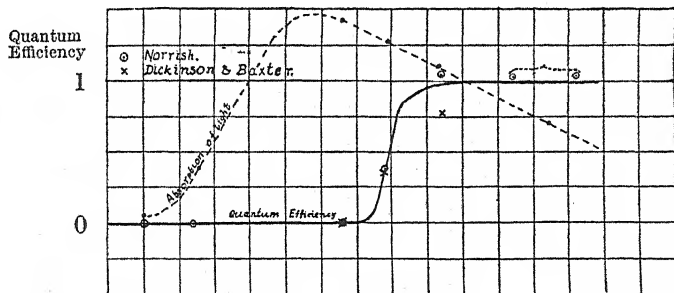


FIG. 66.—The photochemical threshold in the decomposition of NO_2 . By permission of the Chemical Society.

low frequencies, and short wavelengths to high frequencies—is zero. At 4360 Å.U. (in the violet) the light-quanta are just big enough to decompose the NO_2 . The quantum yield then rises rapidly from zero at 4360 Å.U. to two at 3400 Å.U. (which is just in the ultra-violet), and there it remains. The region between 4360 Å.U. and 3400 Å.U. is the photochemical threshold region for this particular reaction.

This photochemical reaction threshold is also a fluorescence threshold. On the long-wavelength side of the threshold, the absorbed light-energy is not used up in decomposing the NO_2 ; instead it is re-radiated as fluorescence. On the short-wavelength side there is no fluorescence.

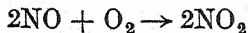
It should be noted that it is not the total energy in the

light that matters, but the amount in each quantum. If the light-frequency is too low, no reaction will occur, however much we increase the intensity of the light; whereas on the high-frequency side of the threshold frequency, every quantum absorbed will cause reaction, no matter how weak the intensity of the light.

It will be seen from Fig. 66 that the threshold in the decomposition of nitrogen peroxide is not absolutely sharp. There is, in general, a twofold reason for this. In the first place, the molecules of the gas possess varying amounts of kinetic energy, for they are in rapid motion. When a molecule has absorbed light, its energy is equal to its original kinetic energy *plus* the energy of the quantum absorbed. If the quantum absorbed is small, the molecules must have a large amount of kinetic energy to begin with, in order that their total energy shall be sufficient to cause decomposition; only a few molecules will have the necessary kinetic energy initially. Whereas, if the quantum is large enough, all the molecules which absorb a quantum will be decomposed.

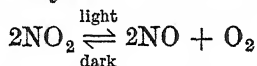
The second reason why photochemical thresholds are not always very sharp can be understood by considering the time that elapses between the excitation of a molecule (by the absorption of light) and its decomposition. If the quantum is large, the excited molecule will possess a lot more energy than the minimum necessary to decompose it, so it will soon break down—its “life” will be short. If the quantum is small, however, the excited molecule may have a relatively long life. This means that it has a considerable chance of losing its surplus energy, either as fluorescence or by collision with other molecules, instead of decomposing; as a result the quantum yield of the reaction begins to fall away gradually on the low-frequency side.

There is another interesting feature about the decomposition of nitrogen peroxide by light. The reverse reaction, the recombination of the nitric oxide and oxygen produced :



also occurs. This reverse reaction is unaffected by light, it is a “dark” reaction; it occurs at the same speed, however strong the illumination.

The state of affairs set up on illuminating nitrogen peroxide is conveniently summarised thus :



The two reactions, the light and the dark reaction, oppose one another. At the beginning of the experiment we start with pure nitrogen peroxide. When we illuminate it, more and more nitric oxide and oxygen are produced ; so the reverse reaction goes on at a faster and faster rate as these two products accumulate. Eventually the dark reaction goes at such a speed that it just balances the light reaction, and the composition of the reacting mixture remains steady. When this happens, it is said that a photochemical steady state has been set up.

This steady state is different from the state of equilibrium set up by the balancing of the rates of two opposing, dark reactions ; it is different because it depends on the intensity of the light used. Suppose we make the light more intense ; then we shall increase the rate of the light reaction, but we shall leave the rate of the reverse reaction unaffected. More nitrogen peroxide will be decomposed than before, and the mixture at the steady state will contain more nitric oxide and oxygen.

INFRA-RED PHOTOGRAPHY.—As has been pointed out already, infra-red light is much less effective in its chemical effects than is ordinary light ; this is because the quanta involved are smaller. Now, taking a photograph involves a chemical reaction, the release of metallic silver from silver bromide. This reaction is ordinarily unaffected by infra-red light ; indeed, it is not affected by all visible light—it is brought about by violet, blue, and green light, but not by yellow or red light. This is because the silver bromide does not absorb yellow, red, or infra-red light.

With an ordinary photographic plate or film it is impossible to photograph a yellow or a red object—it simply comes out black, for the rays from such an object will not affect the grains of silver chloride or silver bromide in the plate. To photograph a yellow or red object satisfactorily, it is necessary to “sensitise” the plate to these rays.

This can be done by impregnating the plate with suitable dyes. What exactly happens we do not know, but the dye absorbs the desired light and in some way passes on the energy of this light to the silver chloride or silver bromide grains. By using the dye, sensitol red, we can record every colour in the visible spectrum, except the deepest reds; plates sensitised with this dye are called panchromatic plates.

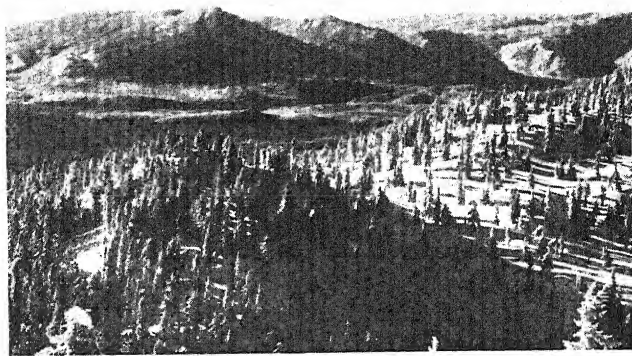
With some dyes we can go a stage further and photograph infra-red rays. The particular dyes used for this purpose belong to the class known as the cyanine dyes; with xeno-cyanine, for example, we can penetrate into the infra-red a distance equal to that between the violet and the red in the visible spectrum.

The value of infra-red photography is that it enables us to "see" many things not visible to the naked eye; our eyes do not respond to infra-red light, but a suitably sensitised plate does.

The longer the wavelength of light, the better it is able to penetrate fog and haze. The small particles of dust, moisture, etc., in the air scatter blue and violet light much more than red light, so red light has a greater penetrating power than blue or violet light; that is why street lamps appear red during a fog. Infra-red light has an even greater penetrating power than red light. With its aid we can "see" objects obscured behind fog or haze. All that is necessary is to take a photograph using an infra-red plate. A suitable filter is used to cut off ordinary light, so that the effect on the plate is due entirely to the infra-red light from the objects being examined.

It is in this way that the surprising long-range photographs of the coast of France from England, and so on, are taken; the record distance is over three hundred miles. Such photographs are of special value in aerial mapping. With ordinary photographs it would be necessary to fly very low to obtain reasonably clear photographs; so that a very large number of exposures would be necessary to cover a large district. With infra-red apparatus, one can fly high and still get clear photographs; each photograph includes a large area of country, so that relatively few exposures are necessary.

PLATE VIII.

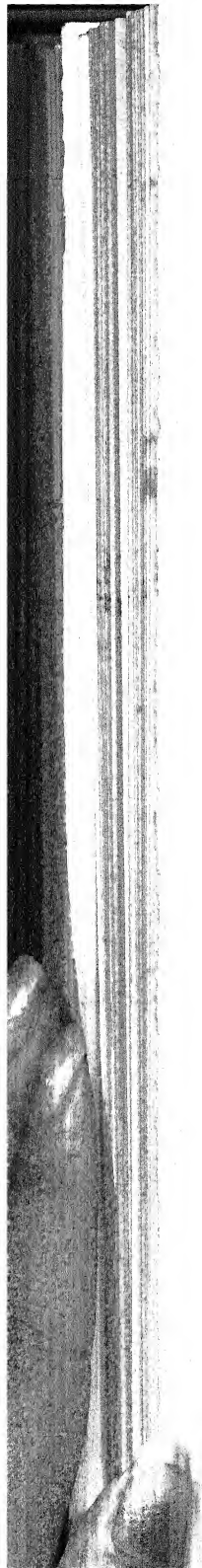


INFRA-RED PHOTOGRAPHY.

Above : Photograph of Bowen Island, British Columbia, taken in the ordinary way.

Below : An infra-red photograph of the same scene. The hills in the background are twelve miles away.

The amount of detail is enormously increased by the use of penetrating infra-red rays. It will be seen that some of the colours come out "wrong."
(By kind permission of Messrs. Ilford, Ltd.)



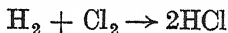
Infra-red photography has been applied, too, to render visible again writing that has been blacked-out. The top layer of ink may consist of different materials from the writing beneath. If the top layer does not reflect infra-red light, while the writing below does, then in an infra-red photograph, the writing will show up through the ink above. Ultra-violet light can be employed on the same principle; usually one or the other enables us to read writing that has been crossed out.

Infra-red photography has important scientific uses as well. It can be used in infra-red spectroscopy, but we cannot yet penetrate as far into the infra-red as we should like for this purpose. Another use is for showing up details, for instance in photographs of insects, not visible in an ordinary photograph.

CHAPTER XVIII

CHAIN REACTIONS

THE quantum yield of a photochemical reaction is often equal to unity or less ; not more than one molecule reacts for each quantum of light absorbed. Sometimes the quantum yield rises to two or three, and this—as we have seen—can be accounted for in a simple manner. But in the reaction between hydrogen and chlorine :



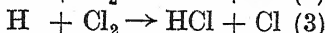
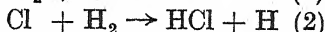
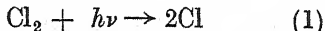
under the influence of light, millions of molecules react for each quantum of light absorbed.

It is evident that some new type of process is involved in this reaction. Nernst suggested the following mechanism :

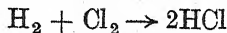
(1) The first process is the dissociation of the chlorine molecules into atoms under the influence of light.

(2) Then each chlorine atom produced reacts with a hydrogen molecule, giving a molecule of hydrogen chloride and an atom of hydrogen.

(3) The hydrogen atom reacts with a molecule of chlorine, forming a molecule of hydrogen chloride and regenerating an atom of chlorine.

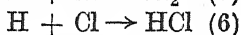
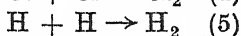
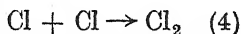


Processes (2) and (3) repeat, alternately, many times, so that a long chain of processes occurs ; each link in the chain generates the atom of chlorine or hydrogen necessary for the next link. The net result of processes (2) and (3) is as we should expect.

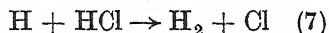


It is important to realise that the chains we are discussing are chains of reactions rather than chains of molecules ; each link in the chain is a chemical reaction.

The chains are not indefinitely long ; in the hydrogen and chlorine reaction they may reach a million links in length, but the chains in most chain reactions are rather shorter than this. There are several ways in which the chains may be broken ; they will be broken by any process that uses up the hydrogen and chlorine atoms, which are essential to the propagation of the chains. Various possible processes are :

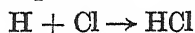


all of which use up hydrogen or chlorine atoms. The reaction :



is also important in slowing down the reaction ; it is the reverse of reaction (2) in the Nernst chain. If we add some hydrogen chloride to the reaction mixture initially we shall favour the occurrence of this reaction (7), and the rate of combination of hydrogen and chlorine will be slowed down—the hydrogen chloride has an inhibiting effect on the reaction.

It might be thought that reactions (4), (5), and (6) would occur every time the right atoms collide. As a matter of fact, they do not. A molecule of hydrogen chloride, for instance, formed by the process :



has an excess of energy and is therefore unstable ; it will simply split up into atoms again. If, however, a third molecule is present when the atoms of hydrogen and chlorine combine, this third molecule may be able to take up the excess energy and so stabilise the hydrogen chloride molecule. The walls of the containing vessel also can frequently stabilise a molecule in this way, so reaction chains are often broken by the walls.

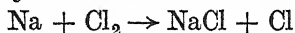
Summarising the features of the hydrogen and chlorine reaction which interest us at the moment :

(1) The reaction is initiated by the formation of chlorine atoms, under the action of light.

(2) This primary process is followed by a series of processes many times repeated, so that a reaction-chain is produced.

(3) The chains can be broken either by reactions occurring in the gas phase or at the walls of the vessel.

Chain reactions not initiated by light are also known. The reaction between hydrogen and chlorine can indeed be initiated in other ways than by illumination. What is needed is to supply the reaction mixture with chlorine atoms ; this can be done by means of such reactions as :



The suspicion that ordinary thermal reactions might prove to be chain reactions first arose in the following way. It is often found that small traces of foreign substances cause a reaction to go much faster. This phenomenon is called catalysis ; there is no particular difficulty in accounting for it ; the molecules simply resort one after another to the catalyst, where they react very rapidly. But the converse process, negative catalysis, is more difficult to explain ; how is it that a small trace of an added substance can slow down a reaction and perhaps almost stop it ? Molecules cannot, in general, exert an appreciable influence on other molecules unless they are in close proximity to them ; so we should not expect that a trace of a foreign substance could affect more than a small proportion of the molecules in a reacting mixture ; there could not be more than a slight slowing down of the reaction.

Yet cases are known in which a very small proportion of impurity will practically stop a reaction. Christiansen suggested that reactions which can be inhibited like this are chain reactions. What the impurity does is to break the chains earlier than they would normally be broken ; if a long chain is broken near the beginning, many molecules which would have reacted will be unable to do so. Quite a small concentration of impurity is able in this way to cut down the average length of the chains considerably, so that the observed rate of the reaction is much smaller.

The oxidation of sodium sulphite solutions by oxygen from the air takes place in the presence of light. It is

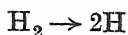
found that small traces of various substances, such as alcohols, inhibit the reaction; so it is deduced that the reaction is a chain reaction. Some confirmation that the alcohols really do inhibit the oxidation by breaking the reaction-chains is afforded by the fact that the alcohols themselves are slowly oxidised during the process. What probably happens is that the reaction-chain involves oxygen atoms; these oxygen atoms normally carry on the chain, but occasionally they oxidise an alcohol molecule instead, so that the chain is broken.

The idea of reaction-chains has been applied to certain kinds of explosive reactions. An ordinary explosion is simply an ordinary reaction going at a very high speed. The speed of a reaction nearly always increases with the temperature; if the reaction itself produces a considerable amount of heat, the surrounding gases may not be able to conduct it away quickly enough; the temperature goes up and up, the reaction goes faster and faster, and an explosion results. The speed of a reaction increases, too, as the pressure is increased; so an ordinary explosion occurs more readily and more violently if the pressure is increased.

But there is another kind of explosion. This kind of explosion has two very definite pressure limits, a lower one and an upper one. Outside the pressure limits, the reaction velocity is very small; within the limits the reaction is of explosive velocity. This behaviour is quite different from that of the ordinary type of explosion, particularly in the existence of an upper pressure limit—an ordinary explosion simply goes more and more violently as we increase the pressure, instead of ceasing altogether at a certain point.

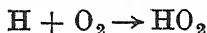
It is this second kind of explosion which has been explained by means of chain reactions. The explosion of mixtures of hydrogen and oxygen may be taken as an example; the reaction-chains are probably built up thus:

(1) Hydrogen atoms are produced from hydrogen molecules:

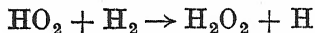


It is very likely that this process occurs on the walls of the vessel containing the gases.

(2) Each hydrogen atom reacts with a molecule of oxygen :



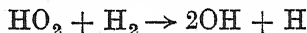
(3) The HO_2 molecule reacts with a molecule of hydrogen, giving hydrogen peroxide and an atom of hydrogen :



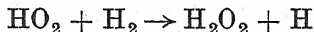
(4) The hydrogen atom formed in process (3) undergoes process (2) again. Chains are formed by the repetition of (2) and (3) a large number of times.

The chains can be broken either at process (2) or process (3). (Of course, each process occurs many times in the chain ; the break may occur at any repetition.) If the H atoms or HO_2 molecules reach the vessel walls they may be adsorbed or they may react there : they are then no longer able to carry on the chain. Thus we see that chains usually come to an end on the surface of the walls.

Sometimes process (3) is replaced by



This happens whenever the HO_2 molecule possesses an abnormally large amount of energy. The result is a branching of the reaction chain ; both the OH molecules, as well as the hydrogen atom, initiate long series of reactions. An important point is that this branching can be prevented if another molecule of any sort is present when the HO_2 and H_2 molecules collide. This third molecule can carry off the excess energy, so that after all the ordinary process



takes place. When this happens, no branching occurs.

If branching occurs at all frequently, the reaction will take place very rapidly. Continued branching proceeds in geometrical progression and increases the velocity of the reaction so enormously that it takes place explosively.

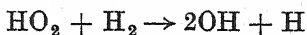
It is this branching of the reaction-chains that is the explanation of the sharp pressure limits observed in explosions of this type : if branching occurs, the reaction is explosive ; if it does not occur, the reaction takes place very slowly. The controlling factors are : (1) the breaking

of the chains on the vessel walls and (2) collision with a third molecule ("ternary collisions") at process (3) in the chain.

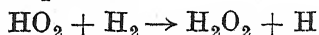
Now, the chains may be broken (usually by deactivation of molecules which would otherwise carry on the chain) either in the gas phase or on the walls of the containing vessel. These two controlling factors are differently affected by the pressure. At low pressures the influence of the walls dominates the reaction; the chains are broken at the walls as quickly as they are formed, so that the reaction proceeds very slowly. As we raise the pressure, the molecules become more crowded; collisions between molecules in the gas phase become more frequent; so that the influence of the walls becomes relatively less important. Amongst the crowded molecules, the links of the chains are close together and branching proceeds apace; the gases explode. If we increase the pressure still further, the ternary collisions at process (3) will occur so often as to render branching a very rare process; the reaction will once again take place slowly.

That this interpretation of the upper and lower critical pressure limits of explosion is correct, has been confirmed in several ways. The lower limit depends on deactivation on the walls, of molecules which would otherwise carry on the reaction-chain. If we decrease the size of the reaction vessel, collisions with the walls will be more frequent, so this factor will be more effective in breaking the chains. Thus the lower pressure limit should be higher when the vessel is small than when it is large—we have to increase the pressure further before the branching of the chains becomes of greater importance than their breaking at the walls. This has been verified experimentally in numerous cases, including the hydrogen-oxygen case already discussed.

We can increase the chance of ternary collisions in the gas phase too; and hence prevent branching of the chains. To do this we add some foreign gas, which does not react with any of the actual reacting gases. Instead of branching by the process:



the excess energy is passed on to the molecules of this added gas and the normal process :



occurs. As a result of this, the upper critical pressure limit is lower ; as the reaction is carried out at higher and higher pressures, explosion ceases at a lower pressure than usual.

If a foreign substance is added, which reacts with one of the substances in the chain, it will be far more effective in breaking the chains than one which merely deactivates molecules in the chain. This is, as we have seen, one of the main causes of the phenomenon of negative catalysis. In the oxidation of sodium sulphite, substances which react with the oxygen atoms in the chains inhibit the reaction by breaking the chains.

This type of negative catalysis is of practical importance in the case of anti-knocks. The action of the internal combustion engine depends on the explosion of mixtures of air and petrol vapour. It is important that the explosion should take place at the right moment, when the piston in the explosion-chamber is at the top of its stroke. Premature explosion leads to " knocking " and must be avoided.

The explosion of petrol vapour is a chain reaction. In order to prevent premature explosion it is necessary to add something to break the reaction-chains and so keep the reaction under control. Lead tetraethyl, $\text{Pb}(\text{C}_2\text{H}_5)_4$, can be used for this purpose ; it is called an anti-knock. It does not interfere with the ordinary explosion of the petrol at the top of the piston stroke, for this is started by actually igniting the gases.

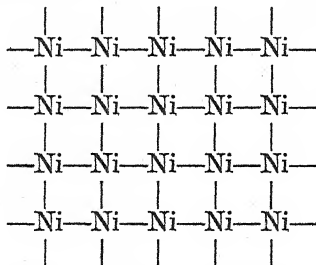
The great value of using a negative catalyst like lead tetraethyl as an anti-knock is that only a very small amount is needed, 1 part in 1,500. This small quantity is able to add about 10 per cent. to the efficiency of the engine.

CHAPTER XIX

ADSORPTION AND CATALYSIS AT SOLID SURFACES

A MOLECULE in the interior of a solid is surrounded symmetrically by other molecules. It is attracted by these surrounding molecules, but there is no net pull on it; the attractions balance one another out. On the other hand, a molecule in the surface of a solid is pulled inwards by the molecules in the interior of the solid, and there are no molecules on the other side to balance these attractions; so there is a net inward pull on the surface molecules. (It is this inward pull which, in the case of liquids, gives rise to the phenomena of surface tension.)

As a result of this inward pull, surfaces contain a considerable amount of energy. There is also another reason why surfaces contain much energy; it applies particularly to metal surfaces. In the interior of a metal, every atom is linked to the surrounding atoms. But the atoms in the surface of the metal are not surrounded on all sides by other atoms; they have each a free valency turned outwards—there is no metal atom to which these free valencies can be attached. The free valencies give metal surfaces many specific chemical properties.

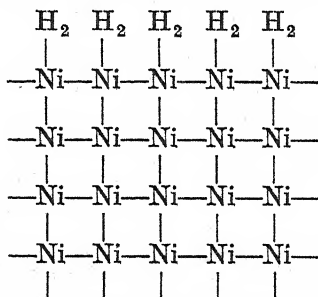


If a liquid or a gas comes into contact with a solid surface, it comes within range of the very powerful forces

acting there. These forces attract the molecules of the liquid or gas, so that the molecules may be held by the surface. In the case of a metal surface, it will probably be definitely the free valencies of the atoms in the surface that "take hold" of the molecules coming into contact with it.

In this way a very thin film, only one molecule thick, of the liquid or gas is attached to the surface of the solid. This is the process known as adsorption. The nature of adsorption depends on the kind of adsorbing surface; two important kinds of adsorption are distinguished.

Adsorption on metals is definitely a chemical phenomenon; chemical forces are involved in the process. The diagram illustrates the sort of thing that happens, the example taken being the adsorption of hydrogen on nickel.



In the interior of the metal the nickel atoms are all linked together. The free valencies of the nickel atoms in the surface layer form links with hydrogen molecules. In this way a sort of two-dimensional compound is produced across the whole surface (the third dimension is only one molecule in thickness). The links between the nickel and the hydrogen are the same as those which exist in the nickel hydrides, except that the nickel atoms are still linked with the other nickel atoms below. The affinity of hydrogen for nickel is not strong enough to break the links between the nickel atoms; so the compound formation does not extend below the surface layer. Carbon monoxide, on the other hand, has a much greater affinity for nickel. Carbon monoxide is able to break the links between the nickel atoms, so that the whole mass is converted into nickel carbonyl, $\text{Ni}(\text{CO})_4$.

This is not a case of adsorption but of the formation of an ordinary compound.

As soon as a layer of gas, one molecule thick, has been adsorbed on the surface, all the free valencies of the metal have been taken up, so that no more gas can be adsorbed. When this happens the surface is said to be saturated. This saturation phenomenon is an important feature of adsorption on metal surfaces.

[The equation connecting the pressure of the gas with the amount adsorbed on the metal can be found in the following way :

Suppose that a fraction σ of the surface is covered by gas. Then a fraction $(1 - \sigma)$ is free of gas. At equilibrium, gas molecules go on to the surface at the same rate as they leave it. The rate at which they go on to the surface is proportional to $(1 - \sigma)$ and to p , the pressure of the gas. The rate at which they leave the surface is proportional to σ . Hence

$$p \times (1 - \sigma) = \sigma \times k$$

where k is a constant. By simple algebra,

$$\sigma = \frac{p}{p + k}$$

This equation brings out the saturation limit. However big p is, σ can never be greater than one; we can never obtain more than a unimolecular layer.]

The other kind of adsorption is known as "pore adsorption." Adsorption by porous substances, such as suitably prepared charcoal and silica gel, is of this nature. The porosity of charcoal gives it a very large surface on which gases can be adsorbed. The surface forces already mentioned attract the molecules of the gas. It is probable that many of the gas molecules are trapped and held in the pores of the charcoal. The trapped molecules have a very restricted freedom of movement, so they are in a quasi-liquid state. The process of pore adsorption is, indeed, analogous to the condensation of a gas rather than to the formation of a chemical compound. In support of this view it is found that the more easily a gas can be condensed, the more easily it can be adsorbed by such substances as char-

coal ; whereas adsorption by metals takes place regardless of ease of condensation.

The large power of adsorption possessed by charcoal is used in many processes. In producing very high vacua, the bulk of the gases is removed from the apparatus by means of pumps and the last traces are removed by adsorption on charcoal ; the charcoal is specially prepared so as to be very porous and hence very good at adsorbing gases. The charcoal is cooled by means of liquid air so as to increase the amount adsorbed of the gases. Charcoal is employed also to remove impurities from solutions—for decolorizing and deodorizing them. It is, for instance, used to remove colouring matter from sugar solutions before the sugar is crystallised out. Another use of charcoal is to reclaim dyes from water. The solution of the dye is agitated with charcoal ; the charcoal adsorbs the dye and is filtered off. The dye is easily recovered from the charcoal by washing it out with alcohol.

The area of the adsorbing surface is a matter of considerable importance. In the case of charcoal and silica gel, the porosity of the material ensures a large surface, so these substances are good adsorbents. A metal surface is not very large when the metal is in bulk. But during use a metal surface often becomes pitted and cracked ; this increases the area, and it is then a much more efficient adsorbent.

The actual adsorbing area is often greater than it appears to be. There are often minute pores in the surface, pores which may be invisible even under the microscope, and these increase the area considerably.

One of the most usual ways of ensuring a large surface is to have the substance finely powdered. The effect of division into small particles may be illustrated by cutting up an apple. When an apple is cut in two the area is increased by the two white circles which are exposed, whilst the total volume remains unaltered. Every additional cut increases the area still further without altering the total volume. Hence a powder has a much greater surface area than the same volume of the substance in bulk.

We can go a stage further and use a colloidal solution of the adsorbing material. A colloidal solution of, say, the metal palladium contains a large number of very minute particles of palladium dispersed throughout the solvent. The particles are so small that they cannot be seen even under the highest-power microscope; their total surface area is, therefore, very great compared with the volume. If we took a little cube, with sides 1 cm. long, and reduced it to particles of colloidal size, we should increase the surface area from 6 square centimetres to several hundred square metres—an increase of about a million times.

Fine precipitates share with colloid particles this great power of adsorption. This is sometimes very troublesome. The fine precipitate adsorbs other substances from the solution from which it has been precipitated, and so upsets any quantitative investigation.

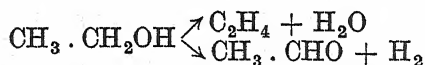
In preparing a material which is to be used for adsorption (or for catalysis) it is often expedient to deposit it on a suitable support. Asbestos, for instance, is used as a support for platinum in making platinised asbestos. The asbestos is soaked in a solution of platinic chloride. It is then heated, when the platinic chloride is decomposed with the formation of free platinum. The platinum is deposited in the pores of the asbestos in a very finely divided state. Platinised asbestos is much more convenient to use than powdered platinum itself, because it is easier to bring large quantities of gases into contact with the platinum in this form.

When it is actually desired to adsorb gases or substances from solution, a substance of the charcoal type is usually employed. Adsorption by metals is put to different uses, namely, to catalyse certain chemical reactions. (Catalysis means the acceleration of a reaction by means of substances which do not actually take part in it; these added substances are called catalysts.) What happens is that the molecules adsorbed by the metal surface are brought into contact with one another and are able to react actually on the surface. For this reason such reactions are known as surface reactions (or sometimes as heterogeneous reactions, in contrast to

homogeneous reactions, which take place throughout the whole of the gas or solution).

Why have surfaces such a high chemical activity? It is due partly to the fact that substances adsorbed on a surface are nearly always at a higher concentration there than they are in the gas or solution from which they came; as we know, chemical reactions are usually accelerated by increasing the concentration. Putting this in another way, the molecules on the surface are brought very close to one another so they are particularly likely to react. There is also another important factor: the molecules on the surface are subject to those large and unequal forces which are characteristic of surfaces in general. These forces distort the molecules and so make them less stable, more ready to react, than undistorted molecules.

It was once thought that the concentration effect alone would account for the high speed at which chemical reactions often take place on surfaces. But it will not account completely for the behaviour of surfaces in catalysing chemical reactions. Alcohol, for instance, can decompose either into ethylene and water or into aldehyde and hydrogen. The reactions are:



The first reaction takes place on an alumina (aluminium oxide) surface at 300°C. , the second on a copper surface at the same temperature.

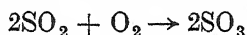
It needs more than a mere concentration effect to account for the two completely different ways of decomposition. The difference in this case is probably due to the fact that an alumina surface adsorbs water readily, while a copper surface adsorbs hydrogen. When alcohol decomposes on alumina, it tends to lose water; the water sticks to the surface, and the rest of the molecule comes off as ethylene, C_2H_4 . On a copper surface, however, hydrogen tends to stick to the surface; so the alcohol molecule breaks into hydrogen and acetaldehyde, $\text{CH}_3 \cdot \text{CHO}$.

In the decomposition of alcohol there is only one substance adsorbed on the surface. We can have, too, reactions

between two or more substances taking place on surfaces. For this to occur both substances must be adsorbed, so that the two kinds of molecules are side by side on the surface. The distortion of the molecules will again be important, rendering them abnormally reactive.

Sometimes other substances may be adsorbed besides those we want to react together ; impurities in the reacting mixture, for example, may be adsorbed on to the catalytic surface. If an impurity is very strongly adsorbed, it will cover up quite a large area of the catalyst surface and prevent the reactants from getting at the surface. When this occurs the reaction slows down a great deal, and the catalyst is said to be poisoned.

The poisoning of catalyst surfaces is a matter of great practical importance. In the manufacture of sulphuric acid by the contact process, a mixture of sulphur dioxide and oxygen is passed over platinised asbestos ; the product is sulphur trioxide :



The finely divided platinum in the asbestos acts as a catalyst for the combination of the two gases. (In modern practice, the platinum is not deposited on asbestos, but on hydrated magnesium sulphate. This is heated strongly, and a porous mass of anhydrous magnesium sulphate, containing finely divided platinum, is obtained.) It is essential to use very pure sulphur dioxide and oxygen in this process ; if there is a small amount of, say, an arsenic compound present, it will be adsorbed on to the finely divided platinum ; this will prevent the sulphur dioxide and oxygen getting on to the platinum surface and the reaction will very nearly stop. This is why it is better to obtain the sulphur dioxide for this process by burning sulphur rather than by burning iron pyrites—the latter is nearly always contaminated with arsenic compounds.

Another example of catalyst poisoning is found in the manufacture of ammonia by the Haber process. This process involves the direct combination of hydrogen and nitrogen in presence of a suitable catalyst. The actual catalysts used are a trade secret, but most of them contain

ferric oxide as one of their most important constituents. The catalyst is poisoned by carbon monoxide, which is usually present as an impurity in the hydrogen used ; the carbon monoxide must be removed from the hydrogen before it is used in the process. [This is done by passing the gas through ammoniacal cuprous formate solution.]

The great difficulty with catalyst poisons is that they have a considerable poisoning action even at quite low concentrations. There need only be enough of the poison present to form a layer one molecule thick over the surface, for it to bring the reaction to a standstill, by preventing the reactants from reaching the catalyst. Thus 1 per cent. of carbon monoxide mixed with the hydrogen in the synthesis of ammonia will slow down the reaction so much that it can no longer be carried out profitably.

Sometimes one of the products of the reaction acts as a catalyst poison, although it is perhaps better to speak of "retardation" of the reaction by the products. The combination of sulphur dioxide and oxygen—a reaction already referred to—affords an example of this. The sulphur trioxide formed during the reaction is adsorbed on to the platinum catalyst ; this hinders molecules of the reactants from getting at the catalyst, and so slows down the reaction.

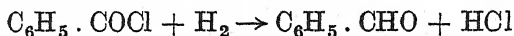
Occasionally even one of the reacting substances themselves may have a poisoning effect. If one of the reactants is very strongly adsorbed, it may form a practically complete unimolecular layer (a layer one molecule thick) over the surface. In this way it will almost exclude the other reactants from the catalyst, so the reaction will be slowed down considerably. A case of such poisoning by one of the reactants is found in the combination of ethylene and hydrogen on a copper catalyst :



Here it is found that increasing the concentration of ethylene actually decreases the rate of the reaction, whereas reactions usually go faster when we increase the concentration of a reactant. The reason is that the more ethylene there is

present, the more nearly is there a complete unimolecular layer of ethylene over the surface of the copper ; the less can hydrogen get at this surface, so the reaction takes place more slowly.

Although catalyst poisoning is generally a troublesome feature, there is such a thing as beneficial poisoning. A partial poisoning of the catalyst is sometimes advantageous because it slows down a reaction to a reasonable rate ; it prevents the reaction getting out of hand. Sometimes, too, a partial poisoning of the catalyst causes a change in the reaction which occurs. For example, benzoyl chloride is reduced by hydrogen, colloidal palladium being used as a catalyst ; the reaction is carried out in solution in benzene. The product formed depends on what impurities are present in the benzene. If ordinary benzene is used, the product formed is benzaldehyde :

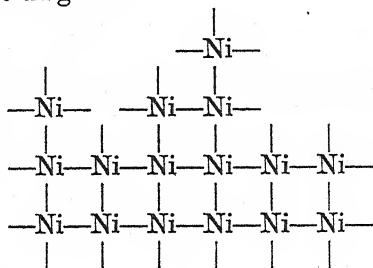


In presence of suitable impurities the product may be benzyl alcohol, toluene, dibenzyl ether, etc. It can readily be imagined that such an effect due to partial poisoning might be beneficial in many cases.

A particularly clear case of such partial poisoning is found in the hydrogenation of (that is, the action of hydrogen on) propyl ketone, piperonal, and nitrobenzene ; the catalyst is colloidal platinum. In the normal course of events all three compounds are hydrogenated. If we add a little carbon disulphide—an inflammable liquid with a smell like rotting cabbage—the catalyst is partially poisoned. We can add just enough carbon disulphide to stop the hydrogenation of propyl ketone, but not the hydrogenation of the other two compounds. A little more carbon disulphide will poison the catalyst a little farther, enough to stop the hydrogenation of piperonal, but not that of nitrobenzene. With a still further addition of carbon disulphide all three reactions will be prevented.

How does this partial poisoning arise ? It has been suggested that the reason lies in the fact that no surface is absolutely uniform. It might be thought that a polished

metal surface is uniform enough, but actually such a surface is quite complex. It usually consists of small crystals of the metal and broken pieces in all possible orientations, with some amorphous material in the interstices. Even a single crystal has corners, edges, and faces, with differing properties. Another way in which non-uniformity may arise is shown in the diagram.



Some of the nickel atoms at the surface have more than one free valency, so they will be more than usually active as adsorbing centres.

There are, then, a number of "active centres" on every surface. When there are several reactions taking place at once on the same surface, the most difficult reaction occurs at the most active parts of the surface. A very small amount of poison may then be introduced. The poison covers the most active centres first, and so stops the most difficult of the reactions whilst the others proceed at the less active parts. The next most difficult reaction is stopped when the next most active centres have been covered by the poison, and so on.

So far we have been considering the interface between a gas and a solid, or between a liquid and a solid. The interface where two solids meet is also of great importance.

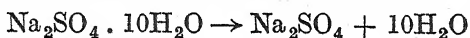
To get such an interface the two solids must be finely divided and thoroughly mixed together; this ensures that the particles of the two solids really are in close contact with one another. This is usually achieved by chemical means, such as precipitating the two solids together from a solution.

Chemical reactions often occur more readily at the reinterface between two solids than they do elsewhere. Sodium

sulphate forms crystals in which it is associated with ten molecules of water of crystallisation, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. Under suitable conditions the salt will slowly lose its water of crystallisation; it will "effloresce." This efflorescence is easy to watch because anhydrous sodium sulphate, Na_2SO_4 , appears on the crystal surface; this anhydrous salt is white and powdery. Faraday found that if a crystal of sodium sulphate is scratched, the efflorescence starts at the scratch and spreads outwards from it. This is explained by supposing that efflorescence occurs best where the hydrated sodium sulphate is in contact with the anhydrous sodium sulphate.

Confirmation of this idea can be obtained by measuring how fast the efflorescence progresses. At first, as more and more of the anhydrous salt is formed, the interface between the hydrated and the anhydrous salt increases in area; so at first we should expect the reaction to increase in speed. But eventually most of the hydrated salt will be used up; after this the interface decreases in area as the efflorescence progresses, and we should expect the reaction to slow down again. This is just what we actually find: at first the reaction goes at an increasing speed, and at the end it goes at a decreasing speed.

Why has an interface between two solids such a high chemical activity? The essential reason is this: if the hydrated sodium sulphate were to lose its water directly, only one chemical reaction would be involved:

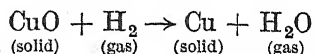


But in presence of anhydrous sodium sulphate, a two-stage process can occur. The water lost by the hydrated salt is not given off at once as water-vapour. In the first stage the water is handed on to the anhydrous sodium sulphate, and it is adsorbed on the surface of this anhydrous salt. The second stage is the loss of this adsorbed water by the anhydrous salt, so that water vapour is given off.

Thus we have a two-stage process instead of a one-stage process. It often happens that such a two-stage process occurs more readily than the corresponding one-stage

process, and if that is so we may find a marked tendency for the reaction to occur at an interface. In the case just mentioned the two-stage process at the interface evidently does take place much more readily than the direct loss of water as vapour by the hydrated sodium sulphate.

The same sort of explanation is available to explain the behaviour of such a reaction as :



(Cu is the symbol for copper, and CuO is copper oxide). This reaction, the reduction of copper oxide to copper, does not take place except at the interface between copper oxide and metallic copper. This case differs from the previous one in that a gaseous substance occurs on both sides of the equation: there is a gaseous reactant, hydrogen, and a gaseous product, water vapour. Here there are several possibilities for the occurrence of a two- or more stage process instead of the simple single-stage process represented by the equation for the reaction. One such possibility is :

- (1) The hydrogen is adsorbed on the copper.
- (2) The hydrogen is passed from the copper to the copper oxide and reacts with the latter, giving copper and water.
- (3) The water is passed from the copper oxide to the copper, and then evaporates off from the copper.

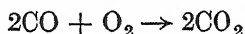
A series of processes like this may well occur more readily than the direct single-stage process.

A still more complex case arises in what is called promoter action. It is often found that a mixture of catalysts is more effective than a single catalyst; when this occurs one catalyst is said to be promoted by the other. [Sometimes a distinction is drawn between "promoter" action and "mixed catalyst" action. In the former case, a small quantity of an added substance helps the main catalyst to do its job better. In the latter case, the two catalysts are used in more or less equal proportions to obtain the maximum effect. It is unlikely that such a classification corresponds to any real difference in mode of action.]

This catalytic activity of mixtures of solids must be due to the interfaces between the two solids. At these interfaces

it is probable, as we have seen, that a several-stage process can take place instead of a simple one-stage process. It is quite likely that a several-stage process exists which occurs more readily than the one-stage process ; in which case the reaction will take place more rapidly at the interface than elsewhere.

Promoter action is of great practical importance. The majority of industrial catalysts are mixtures of two or more substances. An example is found in "hopcalite," a mixture of copper oxide, CuO , and manganese dioxide, MnO_2 . This mixture will bring about the combination of carbon monoxide and oxygen to give carbon dioxide :



at ordinary temperatures. Now carbon monoxide is poisonous—it is the poisonous constituent of ordinary household gas—but carbon dioxide is not. So hopcalite is used in gas masks to convert the poisonous carbon monoxide into the harmless carbon dioxide ; the oxygen necessary is present in the air. It is interesting to note that neither copper oxide nor manganese dioxide alone will bring about the reaction.

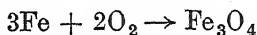
An interesting case of promoter action is found in photography. A photographic plate contains a large number of minute grains of silver bromide ; on illumination, when a photograph is being taken, some of the silver bromide is decomposed, so that metallic silver is set free. This reaction does not take place at all readily unless there is a speck of silver sulphide in the grain of silver bromide. If there is such a speck, the bromide is decomposed much more easily there than elsewhere. This is probably because the reaction can occur in several stages at the interface between the silver sulphide and the bromide.

The sulphide arises by reaction of the silver bromide grains with the traces of sulphur compounds present as accidental impurities in the gelatin. This was discovered originally by the concentration of a garlic-smelling substance from gelatin ; the smell gave a clue to the group of compounds which were involved.

CHAPTER XX

THE CORROSION OF METALS

THE RUSTING OF IRON.—The rusting of iron is one of those apparently simple reactions that turn out on analysis to be distinctly complicated. It might be thought that rusting involved merely the oxidation of iron, a combination of iron and oxygen :



But this simple reaction does not explain what actually occurs.

We have to explain, for example, why it is an advantage to coat iron with zinc, as in the making of galvanised iron. In galvanised iron there is actually no rusting until the zinc is completely corroded away ; the zinc corrodes in preference to the iron. Of course, the protective action of the zinc cannot act over indefinitely large distances ; but if a small area of the iron is exposed to the air through a gap in the zinc, very little rusting will take place there.

A coating of tin, on the other hand, such a coating as is seen in tin cans, actually encourages rusting. So long as the layer of tin covers the whole surface of the iron, no oxygen can get at the iron, and there is no rusting ; this is, indeed, the purpose of coating iron with tin. But even a slight gap in the tin leads to considerable rusting ; when a crack occurs, the iron corrodes in preference to the tin. [Sometimes, however, the tin decreases the amount of rusting of the iron. This anomaly may be due to the formation of a film of oxide on the surface of the iron.]

All this indicates that the rusting of iron is a more complex phenomenon than it appears to be at first sight. How are we to account for the different effects of zinc and tin ? We know—this is a matter of common knowledge—that zinc is electrically negative to iron. Small currents tend to pass

from the iron to the zinc. Now it is the metal of the negative electrode that tends to go into solution; in the Leclanché cell, for example, the zinc is the negative electrode, and this goes into solution. Small currents tend to pass from the positive iron to the negative zinc, so the zinc goes into solution in preference to the iron. Tin, however, is positive to iron, so that small currents tend to pass from the tin to the iron. In this case the iron is the negative electrode; the iron goes into solution in preference to the tin. That is, the iron corrodes first.

We have explained why iron corrodes when it is in contact with tin. Impure iron usually contains accidental spots of tin or other metals, so it rusts readily; pure iron, uncontaminated in this way, does not rust nearly so readily. But pure iron does rust. The reason for the rusting in this case is shown by the following experiment: two electrodes of pure iron are immersed in a solution of an electrolyte; no current passes between the electrodes because they are both of the same material and they are both under the same

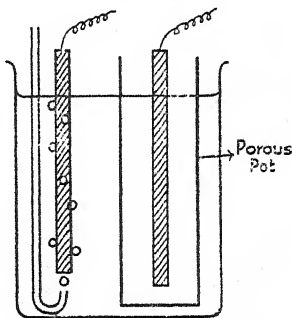


FIG. 67.—Differential aeration.

conditions. Oxygen, or air, is then bubbled through the cell so as to circulate round one electrode but not round the other. The aerated electrode becomes positive relative to the other electrode, and a small current passes from the aerated electrode to the other. This is the very condition necessary for rusting: the aerated electrode in this experiment takes the place of the tin in a cracked piece of tinplate. When a piece of iron is exposed to the weather, air can get at some parts of it better than at other parts; "differential aeration" occurs. Such casual differences are sufficient to set up the small electric currents necessary to start corrosion.

Another experiment shows very neatly just how the rusting of iron actually occurs. A piece of iron is carefully cleaned with emery paper, and a spot of a certain solution

is dropped on it. There are three substances dissolved in this solution: common salt, potassium ferricyanide, and phenolphthalein. The purpose of the common salt is simply to make the solution conducting; the ferricyanide is introduced as a test for the presence of ferrous ions, Fe^{++} —it gives a precipitate of prussian blue when ferrous ions are present; and the phenolphthalein is a test for the presence of hydroxyl ions, OH^- —it turns red when these ions are present. The drop of this solution is left on the iron for an hour or so; by the end of that time it has turned blue at the centre and pinkish round the outside. The blue colour at the centre shows that ferrous ions have been formed there—some of the iron has gone into solution. At the outside of the drop the pinkish colour indicates the presence of hydroxyl ions.

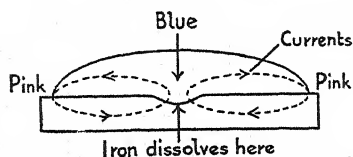


FIG. 68.—An experiment in rusting.

The explanation is that the oxygen of the air can get at the iron better round the edge of the drop than at the centre. Hence there are currents through the iron from the aerated edge of the drop to the unaerated centre; and there are corresponding currents through the solution from the centre toward the edge. Iron goes into solution at the centre as Fe^{++} (ferrous ions) and carries the current outward from the centre; similarly negative hydroxyl ions, OH^- , are formed at the edge of the drop and move inward from there, carrying current in the same direction as the positive ferrous ions. Where the two ions meet a precipitate of ferrous hydroxide, $\text{Fe}(\text{OH})_2$, is formed; this is eventually converted into iron rust, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$.

We can now give, quite generally, the conditions in which the rusting of pure iron occurs. There must be a conducting solution in contact with the iron; the presence of oxygen is necessary; and some parts of the iron must be more aerated than other parts—there must be “differential aeration.”

When iron rusts in air the conducting solution is often water or rain in which carbon dioxide is dissolved. Rain spots on

dissolves carbon dioxide from the air, as it falls ; the carbon dioxide gives a conducting solution.

It will be seen from this account that rusting takes place, not at the points where aeration is greatest, but at the points where the supply of oxygen is least. Thus we find that rusting occurs in the angles of girders and hinges rather than in the more exposed parts. A hinge or girder may be eaten right through by rust at the angle—a most unfortunate circumstance. Another result of this corrosion of the least exposed parts, is that if corrosion once starts it continues in the same places ; the thin coating of rust first formed protects the iron below from full exposure to the air, and so promotes further rusting. In an iron tank which contains a liquid, even a minute crack may cause considerable trouble. Rusting begins in the crack and continues there, owing to the effect of the rust layer in hindering access of oxygen to the crack ; until eventually a hole has been eaten right through the tank.

PROTECTIVE FILMS ON METALS.—Fortunately, the study of the corrosion of metals is not entirely a study of the harmful effects of corrosion. Metals frequently do not corrode when we might expect them to ; and it is possible to treat metals in various ways so as to prevent them corroding.

These beneficial effects are due to the formation of thin films on the surfaces of the metals ; these films prevent the access of air, or other corroding agents, to the metal. The films are often extraordinarily thin, perhaps only one or two molecules thick ; frequently they are thinner than the wavelength of light, so that they have no effect on the colour of the metal. If they are a little thicker than this they may show as “temper colours.” Temper colours are interference colours ; we get such colours whenever an extremely thin film is spread over anything. The colours seen when a thin layer of petrol spreads over water are interference colours.

The formation of temper colours is particularly easy to observe in the case of copper. Clean a piece of copper with emery paper, so as to have a bright, clean surface of copper.

Hold the cleaned copper with one corner in a flame. The temper colours will be seen to run across the copper from the corner which is held in the flame.

Faraday was the first to suggest the existence of protective films on metals. When iron is dipped into concentrated nitric acid it becomes "passive." It will no longer dissolve in dilute nitric acid, for instance, as ordinary iron does; nor will it precipitate copper or silver from solutions of copper or silver salts. Faraday suggested that the effect of the concentrated nitric acid is to produce a thin film of iron oxide over the surface of the iron; this thin film forms a continuous protective covering, so that the iron will not undergo its ordinary reactions.

The most conclusive evidence for the existence of such a film has been obtained by Evans, who succeeded in isolating the film on passive iron. He scratched a line across a specimen of passive iron, and immersed the iron in a saturated solution of iodine in 10 per cent. potassium iodide. The iodine attacked the iron exposed at the crack, but did not affect the film of oxide. After two days the iodine had penetrated from the scratch, right under the film; it was possible to remove the film in flakes 2 or 3 mm. long. In this state the film was transparent and tended to curl up into small rolls; when it was washed it broke up into minute fragments. Evans showed that the film really *was* an oxide film—he showed that it was composed of ferric oxide, Fe_2O_3 .

Even on "active" (ordinary) iron there is a ragged film of oxide; but it is not until there is a film over the whole surface, that the film exerts any protective effect. Ordinarily, the film on iron does not cover the whole surface; but with some metals there is always a complete protective film.

Aluminium is a case in point. When it is made an electrode in an electric cell, it is found to be negative relatively to most metals; it should, therefore, corrode in preference to other metals. But this is not the case. One of the reasons why aluminium is used in making saucepans, etc., is because it is very resistant to corrosion. This

resistance to corrosion is due to the formation of a very thin layer of oxide, which protects the metal below.

If the oxide film can be penetrated or circumvented in some way, aluminium is very reactive, as we should expect. Chlorides, for example, can penetrate the film ; so aluminium corrodes in sea-water. Washing soda is able to dissolve the film and then attack the aluminium beneath ; this is why aluminium pans should not be washed with washing soda. A still further way of getting aluminium into contact with reagents without the oxide film "getting in the way" is to amalgamate the aluminium. This is done by putting the aluminium into a solution of mercuric chloride ; the aluminium displaces some mercury from the solution, and this mercury forms an amalgam on the surface of the aluminium. Aluminium amalgamated in this way is able to decompose water, liberating hydrogen—aluminium amalgam is indeed sometimes used as a drying agent.

Aluminium is used so extensively that many attempts have been made to strengthen the natural oxide film and make the metal even more resistant to corrosion. The addition of a little waterglass (sodium silicate) prevents the corrosion of aluminium by washing soda ; probably a film of aluminium silicate is formed. A more important problem is to prevent the corrosion of aluminium—particularly when it is used in marine aircraft—by sea-water. This can be done by immersing the metal in a bath containing a 3 per cent. solution of chromic acid in water. When a current is passed through the solution in such a direction that the aluminium is the anode, a thickening of the oxide film takes place ; this film is very protective. A great advantage of this method of treatment is that the film completes itself automatically. As soon as any part of the metal is coated with the film, the current ceases over that part of the metal ; the current flows over the uncoated parts only of the metal until they too become coated.

It is very important to be able to produce an artificial film on iron so as to protect the iron from rusting. One method of treating the iron is to heat it in ammonia gas ; a surface film of nitride forms, which is very hard and protective. Another

method is to place the iron in a solution of phosphoric acid ; a very protective film of phosphate forms on the surface.

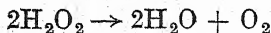
But the most important way of protecting iron from rust is to alloy it with other metals. This is what is done in making stainless steels. Ordinary stainless steels are made by alloying iron with some 15 to 20 per cent. of chromium ; chromium becomes passive more readily than iron, and confers this property on the iron with which it has been alloyed. The oxide film on the alloy forms spontaneously, and heals up very rapidly if it is accidentally broken.

Evans isolated the film on stainless steel, and found that it is considerably thinner than that on ordinary steel. It might be thought that the thinner the film, the less protective it would be ; but the reverse is the case. The film is formed by the attack of some reagent on the metal. If the film is a very protective one, it soon prevents this reagent from reaching the metal and so stifles its own growth ; if a film grows to any appreciable thickness it is, indeed, an indication that its protective action is imperfect.

PERIODIC CORROSION.—Most chemical reactions take place at a steadily decreasing rate, owing to the reactants being gradually used up as the reaction proceeds ; a few take place at a constant rate throughout, and a few go at an increasing rate. But what is altogether more unusual is a reaction which takes place at a rate which alternately increases and decreases.

The solution of a metal in an acid is often a reaction of this type. This was first observed by Ostwald in 1900. He found that when chromium dissolves in dilute acids, the hydrogen evolved in the process does not come off at a steady rate ; it comes off alternately fast and slow. He found that when his original batch of chromium was used up, it was very difficult to obtain such periodic phenomena again ; and indeed a difficulty in reproducing their results at will has beset all workers on this subject.

Another reaction which shows periodic phenomena is the decomposition of hydrogen peroxide, using mercury as a catalyst :



The oxygen is not evolved at a steady rate, but alternately fast and slow. Although the mercury is neither a reactant nor a product of the reaction, yet it is involved in the intermediate stages in some way: a yellow film is alternately formed on its surface and redissolved, in time with the alternate fast and slow evolution of oxygen.

The periods in these reactions are very susceptible to traces of impurities. Very small quantities indeed of a cyanide or of an arsenic compound are sufficient to stop the periods and make the gas evolution quite regular—as little as one part in a million is sometimes sufficient. It is a suggestive fact that arsenic and the cyanides are amongst the most deadly poisons not only to the animal body, but also to surface reactions. Now many natural functions are periodic; the most vital bodily functions, breathing and the beating of the heart, are periodic. It is a matter for speculation whether the poisonous effects of arsenic and the cyanides are directly connected with these periodic phenomena.

The exact reason for the periodicity of so many of the reactions between metals and acids is not known. But similar phenomena are observed in the corrosion of metals which are acting as anodes in electrolytic cells; the mechanism of these reactions has been fully elucidated, and it is highly probable that the reactions we have been considering are periodic for a similar reason.

Before considering this anodic corrosion of metals, we must introduce the idea of current density. The current density at an electrode is simply the amount of current flowing per unit area of the electrode:

$$\frac{\text{Current}}{\text{Area of anode}}$$

Let us take the case of a copper anode in a solution of a chloride. If the current density is low, chloride ions are discharged at the anode and cuprous chloride, CuCl , is formed. Cuprous chloride is insoluble and forms a white layer over the electrode. On the other hand if the current density is high, hydroxyl ions are discharged at the anode

and a black layer, which is probably cuprous oxide, is formed.

It is at intermediate current densities that periodic phenomena appear. At first a white layer of cuprous chloride begins to form on the anode. This film has two effects. (1) It covers up part of the anode and so increases the current density over the uncovered part. (2) It hinders diffusion of the chloride ions towards the copper anode. Both these effects favour the formation of a black oxide film rather than a white chloride film. At a certain point a wave of black sweeps up the anode.

Now, however, the current density falls again and chloride ions can once more diffuse freely towards the anode. But these are the conditions for the formation of a white film again. It is, however, some time before the white film does form again; the oxide film adheres firmly to the copper below, and it cannot dissolve until it has been accidentally broken. The breakage of the film usually occurs at the surface of the solution; when this occurs a wave of white sweeps down the anode. And so the double process goes on; white and black films form alternately.

An essential condition for the occurrence of such periodicity is the setting up of a metastable condition, that is, of a state of affairs which is readily upset but is stable provided the system is not disturbed. The black film is in such a metastable condition. It is not really stable, it should dissolve and give place to a chloride film; but it cannot do so until it is "disturbed" by being broken at some point.

CHAPTER XXI

SURFACE FILMS ON LIQUIDS

SUBSTANCES can usually exist either as solids, liquids, or gases. In the solid state, the separate molecules are fixed in place, they can oscillate backwards and forwards about a central position but they cannot move permanently away from this central position. The molecules in a liquid and a gas are not fixed like this, they can move about freely. A liquid is distinguished from a gas by having a definite bounding surface, whereas the molecules of a gas can diffuse and fill up the whole of the space available for them.

Although a solid or a liquid has a bounding surface, yet it is not impossible for molecules to get through this bounding surface. This is what happens during the evaporation of a liquid or a solid. Of course, the molecules which leave the solid or liquid in this way do not remain in the solid or liquid state ; they form a vapour, which is gaseous in character.

One way of investigating the behaviour of a substance is to examine the effect of temperature and pressure on its volume. If we fix the temperature, we can find the way the volume varies as we alter the pressure, and we can plot a curve to show this variation.

There is an analogy between the behaviour of ordinary substances in three dimensions and the behaviour of surface films in two dimensions. Surface films, like ordinary substances, may be either solid, liquid, or gaseous ; and the three states are distinguished from one another in much the same way in two as in three dimensions.

These surface films are produced when such substances as palmitic acid are introduced on to a water surface. Palmitic acid contains a long paraffin chain, with a carboxyl group, COOH , at one end. The COOH group has a strong attraction for water, whereas the paraffin chain has no

particular attraction for anything. To introduce palmitic acid on to a water surface so that it produces an even layer we proceed as follows. First the water surface is cleaned by moving barriers of waxed paper across it; it is essential to remove any accidental films of grease. A little of the palmitic acid is dissolved in a volatile solvent, such as benzene or light petroleum, and this solution is poured, very carefully, on to the cleaned water surface. The solvent evaporates, leaving a thin, even layer of palmitic acid on the surface.

The molecules of palmitic acid arrange themselves so that their COOH groups are in contact with the water, while their paraffin tails are pointing upwards out of the way. According to this view, it should

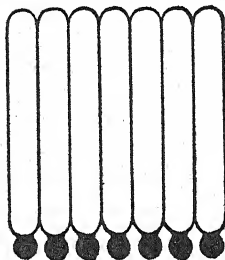


FIG. 69.—Palmitic acid molecules on a water surface. The black blobs represent COOH groups. The white strips represent long paraffin chains.

be impossible to obtain a layer of palmitic acid, oriented in this way, more than one molecule thick. If there were more than enough molecules to form such a layer, not all of them could have their COOH groups in contact with the water. As a matter of fact, if there is too much palmitic acid, the excess simply evaporates off. The molecules whose COOH groups are not held by the water are not restrained like those

molecules whose COOH groups are held, and they are free to evaporate.

It has already been mentioned that one way of investigating ordinary substances is by determining how their volume changes when we alter the pressure. We can carry out analogous experiments with our surface films, and indeed this is one of the most important methods of investigating such films. Instead of volume we must measure the area of the film—it is easy enough to see that. But what is the analogue in two dimensions, of the pressure in three dimensions? If we place a barrier across the surface with the film of palmitic acid on one side of it, the molecules of palmitic

acid will collide with the barrier and exert a force on it ; just as the molecules of a gas exert a force by colliding with the walls of the containing vessel. The pressure in three dimensions is the force over each unit of area of the walls : the surface pressure in two dimensions is the force over each unit of length of the barrier.

Langmuir was the first to devise a means of measuring this surface pressure. In such experiments a long trough filled with water is used ; the palmitic acid or whatever substance is being investigated is introduced on to the water in this trough. At one end of the trough there is a swinging barrier. On one side of this barrier there is a clean water surface and on the other side, the surface film. This surface

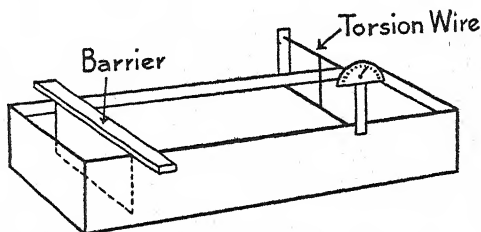


FIG. 70.—The Langmuir trough.

film exerts a surface pressure on the barrier, but the clean water does not. To measure the surface pressure due to the film, the swinging barrier is held in place by means of the torsion in a wire ; the torsion just balances the surface pressure, so that by measuring the torsion we can get a measure of the surface pressure.

We want to see what effect changing the area has on the surface pressure (just as, in three dimensions, we find the effect on the pressure, of changing the volume). For this purpose the trough is fitted with a movable barrier. This barrier can be moved up or down the trough so as to change the area available for the film.

It is important that none of the barriers should leak, that none of the material in the surface film should be able to get past them. One way of preventing this is to have an air jet just between the barrier and the side of the trough ;

this blows back any of the film which tries to get past. A better method is to have a light ribbon of platinum between the barrier and the trough, as shown in Fig. 71.

With this apparatus we can, then, investigate how the surface pressure changes when we decrease the area available for the film. In the case of palmitic acid we get a curve such as the one shown in Fig. 72. If there is ample room for the film of palmitic acid, then there is no pressure on the swinging barrier. As we decrease the area, however, the molecules are squashed up closer and closer together. There comes a point where the whole of the surface is covered

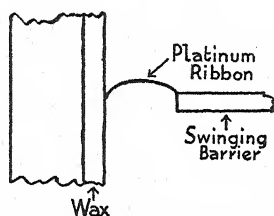


FIG. 71.—A device for preventing leakages at the sides of the swinging barrier.

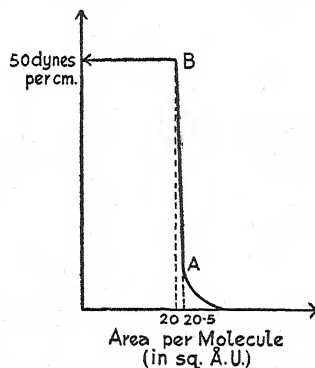


FIG. 72.

with palmitic acid; this occurs when there is a space of 20.5 square Ångström units available for each molecule of palmitic acid. (The Ångström unit is the unit of length used when very small lengths have to be measured; it is equal to the hundred millionth part of a centimetre. The square Ångström unit—often written “sq. Å.U.”—is the area of a minute square with sides one Ångström unit long.) At this point the molecules are all touching one another, so if we try and compress the film any further the film will resist the compression. In other words, it will exert a surface pressure.

Between the points A and B in the diagram we are steadily compressing the film. Although the change in area per molecule is only from 20.5 to 20 sq. Å.U. per molecule, yet

there is an enormous increase in surface pressure. At A the surface pressure is not far off zero; at B it is about 50 dynes per centimetre. The fact that there is practically no change in area during this increase in surface pressure shows how difficult it is to compress the palmitic acid molecules once they are in contact.

Somewhere in the region of B the film breaks down and begins to crumple. The molecules can no longer stand the strain and some of them are forced out of the unimolecular layer. (This phenomenon may be seen on a large scale when there is an obstruction in a stream. A layer of dust collects on the surface near the obstruction and finally wrinkles and crumples.)

It is of interest to find out the exact position of the point at which the molecules are just in contact, where the surface pressure begins to increase very rapidly. The value of such information is that it tells us something about the actual sizes of molecules.

It is found that it does not matter how long the paraffin chain is, A always occurs when there is 20.5 sq. Å.U. available for each molecule.

This is because the molecules are arranged with their COOH groups in the water and their paraffin tails in the air, more or less perpendicular to the surface. The length of the paraffin chain does not, therefore, affect the closeness of the packing—longer and shorter molecules take up just as much room on the surface. This is, indeed, one of the lines of evidence that goes to show that the paraffin chains are nearly perpendicular in the surface.

In the films formed by the fatty acids—the series of compounds like palmitic acid in which there is a COOH group at the end of a long paraffin chain—the paraffin chains are in contact with one another. If there is a very large group at the end of the chain, it is the end-groups rather than the chains which will be in contact. For

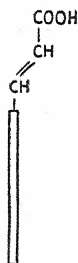


FIG. 73.—The $\alpha\beta$ -iso-oleic acid molecule. The strip represents a long paraffin chain.

instance, in $\alpha\beta$ -iso-oleic acid, the end-group is : $-\text{CH}=\text{CH}-\text{COOH}$. This group is bent round at the double bond so that it takes up a lot of room in the surface. It is found that there is a complete unimolecular layer of this acid when there is 28 sq. Å.U. available for each molecule—a much greater area than the 20.5 sq. Å.U. taken up by the palmitic acid molecules.

The film of $\alpha\beta$ -iso-oleic acid, unlike a palmitic acid film, is fairly easy to compress. The reason for this is evidently that the end-group is gradually straightened out during the compression. This can go on until the area is 20.5 sq. Å.U. per molecule. Then the paraffin chains are in contact and the film is just as difficult to compress as one of palmitic acid (Fig. 74).

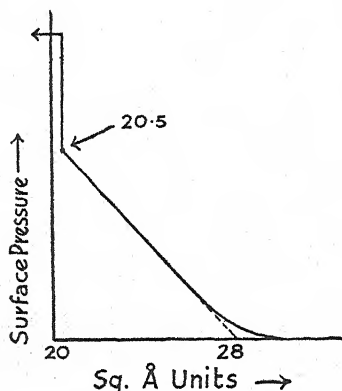


FIG. 74.

The palmitic acid film is of the nature of a two-dimensional liquid. It is very difficult to compress, just like an ordinary, three-dimensional liquid. The molecules in it are not fixed in place, but move about like those of a liquid. We can show this by sprinkling a little talc powder

on the surface; the particles in the powder are carried about over the surface by the motion of the molecules in the film.

But the most important evidence that the film is liquid comes from a consideration of the fact that it has a definite surface vapour pressure. If we increase the volume available for an ordinary liquid, part of the liquid will evaporate. There will then be two phases present, a liquid and a vapour. The latter will be at a definite pressure, the vapour pressure of the liquid. If we increase the volume still further, this pressure will not change but more of the liquid will evaporate to fill up the extra space available. This will go on until the whole of the liquid has evaporated, and there is only the vapour present.

Thus a liquid is characterised by a definite vapour pressure. In the same way the film of palmitic acid is characterised by a definite surface vapour pressure. To the right of A in Fig. 72 there is more room on the surface than the minimum needed for a unimolecular layer. Nearly all the molecules aggregate into "islands" on the water surface, with spaces of practically clear water between the islands. As the available surface is reduced the islands come together until there is a complete unimolecular layer.

But the spaces between the islands are not quite clear of molecules. A few molecules evaporate from the islands and form a two-dimensional vapour in these spaces. (This two-dimensional evaporation into the spaces between the islands is, of course, distinct from the ordinary three-dimensional evaporation of the film into the air above.) This vapour has a definite vapour pressure of 0.04 dyne per centimetre; the curve in Fig. 72 does not fall quite to zero to the right of A. This vapour pressure remains constant as we increase the area right up to the point when all the liquid in the islands has evaporated (Fig. 75).

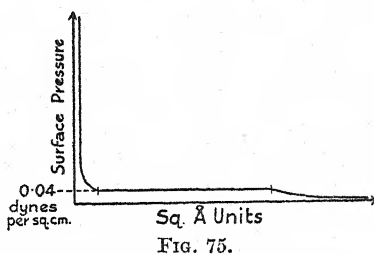
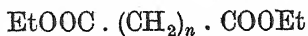


FIG. 75.

Some films are like two-dimensional solids rather than liquids. The two kinds of film can be distinguished by dusting them with talc or some other light powder. The talc hardly moves about at all on a solid film, whereas the molecules in a liquid film carry the powder about as they move. Solid films have, too, a certain amount of rigidity, just like ordinary solids. Substances with very long paraffin chains generally give solid films.

Gaseous films too are known. The most perfect gaseous films are formed by the esters with the formulæ :



where $n = 10$ or 11 . Both the end-groups, COOEt , are

attracted by the water, so the molecules lie flat in the surface. There is thus no possibility of their packing together in a manner like that of the molecules in a palmitic acid film. Instead, the separate molecules move about independently in the surface just like the molecules of a gas. They spread themselves evenly over the surface, however large the area available ; there is no such thing as aggregation into islands giving a definite surface vapour presence.

[“ Perfect ” or “ ideal ” gases follow the law :

$$PV = RT$$

where P is the pressure, V is the volume, T is the absolute temperature, and R is a constant. There is a similar equation for ideal gaseous films :

$$FA = kT$$

where F is the surface pressure, A is the area, T is the absolute temperature as before, and k is a constant. If the equations apply to one gram-molecule in each case, then :

$$k = \frac{2}{3} R$$

Of course, real gases deviate from the equation followed by ideal gases. In just the same way real gaseous films deviate from the equation followed by ideal gaseous films : the deviations are of the same nature in the two cases, although they are proportionately larger for films than for three-dimensional gases. Just as real gases tend towards ideal behaviour as the pressure is reduced, so do gaseous films tend towards ideal behaviour as the surface pressure is reduced.]

Gaseous films are formed most readily when the molecules in the film are attracted at two points, not too close together in the molecule, by the water beneath. An interesting result of this is found in the case of oleic acid. Oleic acid is a long-chain acid with a COOH group at one end ; in the middle of the molecule there is a double bond, $-\text{CH} = \text{CH}-$. Water simply attracts the COOH group, so the film is a liquid one, like that of palmitic acid. When a little potassium permanganate is dissolved in the water, the double

bond as well as the COOH group is attracted. This is just the condition for a gaseous film, and it is actually found that the film is gaseous in presence of permanganate.

So far our films have behaved in a manner parallel to the behaviour of substances in three dimensions. There is, however, nothing analogous in three dimensions to what are called "expanded films." Films of this sort are of very frequent occurrence.

Suppose we heat up a three-dimensional liquid, keeping the pressure constant; if we heat it in the air, the pressure will be constant and equal to the atmospheric pressure. Then the volume of the liquid will increase, but quite slowly. If we do the same thing with a liquid film—heat it up, keeping the surface pressure constant—then at first there is a slow increase in area, analogous to the slow increase in volume of an ordinary liquid. But there comes a point when the area begins to increase rapidly over a range of about $10^{\circ}\text{C}.$; the area roughly doubles itself during this quite small increase in temperature. This is followed again by a relatively slow increase in area.

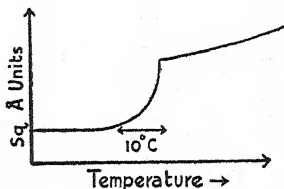


FIG. 76.—The "expansion" of a surface film.

This phenomenon, the quite rapid doubling of the area, is called the expansion of the film. Quite what happens during the expansion of a liquid film in this way is not certain. It has been suggested that the heads of the molecules—such as the COOH groups, for instance—tend to hold the molecules together, but the paraffin chains tend to disrupt them; there is a struggle, as it were, between the liquid state and the gaseous state. This accords quite well with the fact that "liquid expanded films" resemble liquid films in having a certain amount of coherence, and in having a definite surface vapour pressure; but yet the molecules have some of the independence of molecules in gaseous films.

There are also "vapour expanded films." These films are distinguished from liquid expanded films in not having a definite surface vapour pressure. They resemble the liquid

expanded films in being intermediate in behaviour between the liquid and the gaseous state.

Summarising, the following different kinds of films are known :—

Condensed Films.—Condensed films may be either solid or liquid ; the two kinds are distinguished by dusting the surface with talc. They are difficult to compress and they are characterised by a definite surface vapour pressure. They do not spread themselves evenly over the available surface, but aggregate together as “ islands.”

Gaseous Films.—The molecules move about independently and spread themselves evenly over the whole of the available surface. There is no definite surface vapour pressure.

Expanded Films.—Expanded films are intermediate between gaseous and liquid films. The molecules have a certain amount of coherence, but not so much as the molecules in a true liquid film. Liquid expanded films are distinguished from vapour expanded films because they still possess a definite surface vapour pressure.

CHAPTER XXII

WHAT IS AN ACID ?

It has always been a difficult matter to define just what an acid is, even though one knows the properties of substances which are distinctively acid. Thirty years or so ago an acid was defined as a substance which ionises to give hydrogen ions, H^+ . The corresponding definition of a base was a substance which ionises to give hydroxyl ions, OH^- . The terms acid and base were restricted to neutral molecules ; ions, which are molecules with charges, were never described as acids or bases.

In 1923 a new and more general definition of acids and bases was proposed. This new definition has not superseded the older one in ordinary everyday usage, but it is more useful in the discussion of the speed of reactions involving acids and bases.

According to this more general idea an acid is any substance which is a source of hydrogen ions, H^+ ; this definition includes acids in the old sense of the term, and it includes as well many ions which can act as sources of hydrogen ions. The new definition of a base is any substance which can take up hydrogen ions. According to these definitions, acetic acid, $H\bar{A}c$, for example, remains an acid because it is capable of ionising into H^+ and $\bar{A}c^-$. Sulphuric acid, H_2SO_4 , is a more complicated case. It ionises, as a first stage, into H^+ and HSO_4^- ; so sulphuric acid is still an acid under the new definition. This ionisation is reversible : the HSO_4^- ion can combine again with a hydrogen ion, giving H_2SO_4 . HSO_4^- is, therefore, a base, because it can take up the hydrogen ion. But there is a further stage of ionisation by which the HSO_4^- ion yields the two ions H^+ and SO_4^{2-} ; the HSO_4^- ion is, therefore, an acid, because it can yield up the hydrogen ion. Hence it appears that the

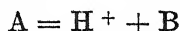
HSO_4^- ion is both an acid and a base ; it can both accept and yield up hydrogen ions.

The hydroxyl ion, OH^- , is itself a base, because it can take up a hydrogen ion and become a molecule of water, H_2O . It is the hydroxyl ion that is the actual base present in a solution of sodium hydroxide, NaOH , for instance. Formerly it was said simply that sodium hydroxide is a base ; the modern definition definitely associates the basic properties with the hydroxyl ion rather than with undissociated NaOH molecules.

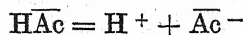
The strength of an acid is measured by the readiness with which it yields up hydrogen ions ; the strength of a base is measured by the readiness with which it takes up hydrogen ions. Thus acetic acid is a weak acid, because it does not readily yield up a hydrogen ion, giving the acetate ion. The acetate ion, on the other hand, is a strong base, because it readily takes up a hydrogen ion giving un-ionised acetic acid. Of course, these are two ways of saying the same thing ; if acetic acid is a weak acid, it follows that the acetate ion is a strong base.

In the case of hydrochloric acid a different situation arises. Un-ionised HCl molecules are very rare in a solution of hydrochloric acid, so HCl molecules are evidently very ready to yield up a hydrogen ion ; they are strongly acid. The chloride ion, Cl^- , is correspondingly very unready to take up a hydrogen ion to give an HCl molecule ; it is a very weak base.

We can generalise these statements by means of the equation :

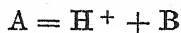


Here A is an acid, and B is the base it forms on yielding up the hydrogen ion. A, for instance, may be acetic acid, HAc , and B the acetate ion, Ac^- :



The acid A and the base B may be either neutral molecules or ions : indeed, one of them, at least, must be an ion, to balance the positive charge on the hydrogen ion.

An acid and a base related according to the equation :



are said to be conjugate to one another. The acetate ion is the conjugate base to acetic acid ; acetic acid is the conjugate acid to the acetate ion. If the acid is strong, then the conjugate base is weak ; for if the acid readily loses a hydrogen ion, then the conjugate base does not readily take one up—a substance cannot have the contradictory properties of readily breaking down into ions and being almost completely un-ionised. We have already had two examples of this : acetic acid is a weak acid, but the conjugate acetate ion is a strong base ; hydrochloric acid is a strong acid, and the conjugate chloride ion is a weak base.

Water occupies an interesting position in the modern theory of acids and bases : it is both an acid and a base. It is an acid because it ionises to H^+ and OH^- ; that is, it is a source of hydrogen ions. It is a base because it can take up a hydrogen ion and become H_3O^+ .

We have been speaking so far as though hydrogen ions could exist as separate entities, as H^+ . But this does not happen (except under exceptional conditions, as in electric discharges through gases) ; in water they are hydrated to H_3O^+ , and in general they are always united to some other atom or group of atoms.

This complicates the question of acids and bases in a most interesting way. When an acid yields up a hydrogen ion, the ion is *at once* taken up by a base ; unless a base is present to do this the acid will be unable to yield up the hydrogen ion. This means that an acid cannot act as an acid except in presence of a base ; equally a base cannot act as a base except in presence of an acid.

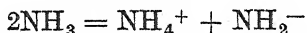
This is why hydrogen chloride, HCl , does not ionise in the pure state : there is nothing to take the hydrogen ion from it. If water is present, hydrogen chloride can ionise at once ; water is a base and can take up the hydrogen ion to give H_3O^+ .

Water is, as we have seen, both an acid and a base ; so

it can ionise on its own, without the addition of any other acid or base ; it ionises thus :



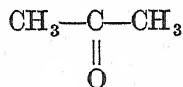
Ammonia, too, is both an acid and a base. Liquid ammonia—real liquid ammonia, obtained by condensing the gas, not the solution in water used for domestic purposes—ionises thus :



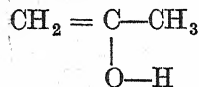
One molecule of ammonia acts as an acid, giving up a hydrogen ion and forming the amide ion, NH_2^- ; the other acts as a base, taking up a hydrogen ion and forming the ammonium ion, NH_4^+ .

So far as we have gone, the new theory of acids and bases has done no more than systematise our knowledge ; it has added nothing to what was known already. For example, the theory describes the chloride ion as a very weak base ; this is only another way of saying that hydrochloric acid is almost completely split up into ions when it is dissolved in water. The new theory has, however, led to considerable advances in the study of catalysis by acids and bases.

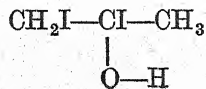
Many reactions are catalysed, that is to say they are accelerated, by acids and bases. The reaction between iodine and acetone is an example of such a reaction. Acetone has the formula :



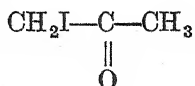
In the first stage of the reaction acetone changes into :



(the enolic form). It will be seen that a hydrogen atom has moved from one of the carbon atoms to the oxygen atom. It is this stage that controls the speed of the reaction as a whole. It is followed by the addition of a molecule of iodine, I_2 , giving :

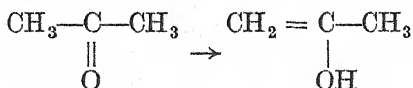


and then by the loss of a molecule of HI, so that the final product is :

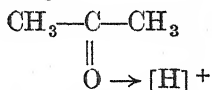


The second and third stages do not concern us at the moment —although they are essential to the practical measurement of the speed of the first stage.

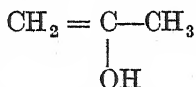
Let us look again at the first stage :



How does the hydrogen atom get from the carbon to the oxygen ? The answer is that the hydrogen atom that leaves the carbon atom is not the same hydrogen atom that turns up on the oxygen. A hydrogen ion is first of all attached to the oxygen atom, giving :



and then a hydrogen atom is removed from the carbon atom, giving :



(A necessary rearrangement of valencies occurs at the same time : the double bond changes its position.) Actually the two processes, the addition of the hydrogen atom to the oxygen atom, and the removal of a hydrogen atom from the carbon atom, must occur almost simultaneously, not one after the other.

For such a reaction to occur, the presence of both an acid and a base is necessary. An acid is required to give up a hydrogen atom to the acetone ; and a base to take one off again in a different part of the molecule. The modern theory of acids and bases is exactly fitted to explain such reactions as the one we have just been discussing.

The necessity for the presence of both an acid and a

base has been demonstrated, very neatly, by Lowry. He investigated a reaction known as the mutarotation of tetramethylglucose; this reaction can be followed, its speed determined, by means of a polarimeter. He showed that the reaction does not take place when the tetramethylglucose is dissolved in pure meta-cresol; meta-cresol is a very weak acid. Nor does it take place when the tetramethylglucose is dissolved in pure pyridine, which is a weak base. But with a mixture of meta-cresol and pyridine the reaction does take place rapidly. This demonstrates in a striking way the necessity for the presence of both an acid and a base in such reactions.

Of course, most of the reactions catalysed by acids and bases have been investigated in aqueous solution. Water is both an acid and a base, so the reactions will take place without the addition of any other substance to act as a catalyst.

The importance of the modern view of acid-base catalysis is that it indicates that *any* substance which is an acid or a base will influence the speed of a reaction which is catalysed by such substances. We must take into consideration every acid and base present. For instance, suppose we find the speed of the reaction in presence of acetic acid, and then add sodium acetate to cut down the concentration of hydrogen ions (or rather H_3O^+ ions). The addition of sodium acetate will involve not only the cutting down of the concentration of hydrogen ions, but also the addition of acetate ions; acetate ions are basic and consequently catalyse the reaction. So the sodium acetate has a double effect; the early investigators considered only the former effect, the decrease in the concentration of hydrogen ions.

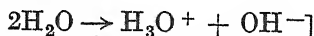
CHAPTER XXIII

CONDUCTIVITY OF SOLUTIONS : THE IONIC ATMOSPHERE

COMMON salt consists of positive sodium and negative chloride ions. These ions attract one another electrostatically ; but in spite of this attraction the ions still have considerable freedom of movement when common salt is dissolved in water. For one thing the water serves to lessen the attraction (by virtue of its high dielectric constant) ; and besides, each ion has a sheath of water molecules which helps to protect it. Thermal agitation keeps the ions in a state of continual rapid motion.

The fact that the ions move about freely has important consequences. If an external electric field is applied to a solution of common salt—this is what is done in electrolysis—the positive sodium ions are attracted toward the negative electrode (the cathode), and the negative chloride ions toward the positive electrode (the anode). When the chloride ions reach the anode they are neutralised and become ordinary, un-ionised atoms of chlorine ; these atoms combine together to give chlorine molecules, Cl_2 , which are then given off at the anode as chlorine gas. At the cathode the sodium ions are neutralised and become ordinary sodium atoms ; they instantly react with water, sodium hydroxide is formed, and hydrogen is given off. [This is rather an inexact way of expressing what occurs at the cathode ; the final products *are* sodium hydroxide and hydrogen, but they are probably produced by somewhat different processes. Water contains hydrated hydrogen ions, H_3O^+ , and the corresponding hydroxyl ions, OH^- . It is the H_3O^+ ions that are neutralised at the cathode rather than the sodium ions. When they are neutralised they give water molecules and atoms of hydrogen ; the atoms react to give hydrogen molecules, which are given off as a gas. The

sodium ions, meanwhile, are moving toward the cathode and tend to accumulate there; so that round the cathode there are sodium ions and hydroxyl ions—a solution of sodium hydroxide, in fact. There are actually very few H_3O^+ ions present in water, and it might be thought that they would soon be used up. This is not so; as they are removed they are continually replaced by the ionisation of more water molecules:



A solution of common salt conducts electricity on account of the two streams of ions: chloride ions carrying negative charges toward the anode, and sodium ions carrying positive charges toward the cathode. This double stream of ions in opposite directions forms the electric current. So far as the external circuit is concerned, the stream of negative charges in one direction has just the same effect as the stream of positive charges in the opposite direction—the flow of electricity is the same in both cases.

In measuring the conductivity of a solution we actually refer our results to the amount of electricity that a small cube of the solution, with sides one centimetre long, would conduct from one face to the opposite face in a second, there being a difference of potential of one volt between the opposite faces. This amount of electricity is called the specific conductivity of the solution. Of course, we do not actually use a centimetre cube of the solution; we use any convenient amount and calculate from this what the conductivity of our unit cube would be.

From these conductivity measurements we want to disentangle three quantities. The specific conductivity evidently depends on:

(1) The number of unit charges on each ion; ions with two charges carry twice as much electricity as ions with one charge.

(2) The actual number of ions in the solution (that is, the number per cubic centimetre); if the number of ions is doubled, the amount of electricity carried by them is doubled.

(3) The speed of the ions; if the speed is doubled, twice as much electricity traverses the solution in a second.

The measured conductivity is the product of these three quantities ; it should be clear that if each of them were doubled the quantity of electricity carried would be increased $2 \times 2 \times 2 (= 8)$ times. The actual conductivity is the sum of several such products, one such product for each kind of ion present in the solution. In addition, we must multiply the sum of these products by a constant depending on the particular units we choose.

It is in this way that the specific conductivity is made up. In quoting values of the specific conductivity, we must state the solute, the solvent (unless it be understood that the solvent is water), and the concentration.

When we come to consider more carefully the quantities involved in the specific conductivity, there is no difficulty about the number of unit charges on the ions ; we know that the sodium ion has one charge, the calcium ion has two charges, the phosphate ion has three, and so on. The actual number of ions per cubic centimetre of the solution is a more difficult matter, because it depends on two factors (two quantities that have to be multiplied together). It depends on the concentration of the solute—on the total number of molecules present in a cubic centimetre of the solution—and it depends on what fraction of these molecules is split up into ions. This fraction is called the degree of ionisation (or, sometimes, the degree of dissociation). The degree of ionisation varies greatly with different substances. A strong electrolyte, like common salt, is almost completely ionised (there is evidence of this quite apart from measurements of its conductivity) ; a weak electrolyte, like acetic acid, is only partially ionised in solution.

The speed of the ions is also a complicated matter. According to the old theory the speed is independent of the concentration of the solute : ions were assumed to move as quickly in a strong solution as in a weak one. It is now known that the speed of the ions is greater in a weak solution than in a strong one.

We are not particularly interested in the effect on the conductivity of the mere decrease in the number of molecules on dilution. If we dilute a solution to half its strength

we shall thereby halve the number of molecules ; the conductivity will decrease for this reason alone, quite apart from any change in the degree of ionisation or in the speed of the ions. It is just the latter two effects that are interesting, so we want to get rid of changes due merely to a change in the actual number of molecules. We can do this by referring our results to the same number of solute molecules in each case ; we consider throughout a quantity of solution which contains one gram-equivalent of the solute. (Thus with common salt we have the atomic weights : sodium 23 and chlorine $35\frac{1}{2}$, so that $58\frac{1}{2}$ grams of common salt would be considered throughout.) The conductivity of such a quantity of solution, containing one gram-equivalent of the solute, is called the equivalent conductivity. The only difference between this and the specific conductivity lies in the quantity of the solute considered ; in the former case we are considering a fixed amount of solute, in the latter case we are considering a varying amount. The equivalent conductivity is simply equal to the specific conductivity multiplied by the number of cubic centimetres of the solution which contain one gram-equivalent of the solute.

To make this point clear : if we dilute the solution until it is half as concentrated, we thereby halve the number of molecules per cubic centimetre. This alone introduces a factor of a half into the specific conductivity. The number of cubic centimetres containing one gram-equivalent has been doubled by the dilution. Hence when we multiply the specific conductivity by this number, we eliminate the factor of a half ($\frac{1}{2} \times 2 = 1$).

[The specific conductivity, σ , is given by

$$\sigma = \frac{\alpha}{1,000V} (u_C + u_A)F$$

where α = degree of ionisation ; V = dilution (the number of litres containing one gram-equivalent of the solute) ; u_C and u_A = actual velocities, in centimetres per second, of the cation and anion ; F = the Faraday = 96,500 coulombs.

The equivalent conductivity, Λ , is defined by

$$\Lambda = 1,000V \times \sigma$$

Hence,

$$\Lambda = \alpha(u_C + u_A)F$$

This depends on the concentration (*i.e.*, on V) only in so far as α and u_C and u_A depend on it.]

We can, then, consider the effect of the concentration on the degree of ionisation and on the speed of the ions. It is convenient to consider first a solution which is completely ionised. Complete ionisation occurs when the solution is infinitely dilute; so that by considering the conductivity of an infinitely dilute solution we can obtain information about the speed of the ions—direct information, uncomplicated by the possibility of incomplete ionisation, etc. Of course, we cannot measure the equivalent conductivity of an infinitely dilute solution directly. But we can measure it for a series of increasing dilutions, and we find that it advances towards a definite limit. This limit is called the conductivity at infinite dilution.

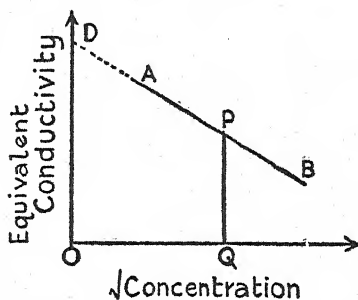


FIG. 77.

In the diagram the equivalent conductivity is plotted against the square root of the concentration; AB is the resulting graph. For any point P , OQ represents the square root of the concentration, C , and PQ represents the equivalent conductivity at concentration C . BA is continued backward until it meets OD at D . Here the concentration is zero, and the dilution is therefore infinite. OD represents the conductivity at infinite dilution, when the solution is completely ionised.

[The conductivity at infinite dilution is written Λ_0 . Since $\alpha = 1$ at infinite dilution,

$$\begin{aligned}\Lambda_0 &= (u_C + u_A)F \\ &= U_C + U_A\end{aligned}$$

where $U_C = F \times u_C$, and $U_A = F \times u_A$.

U_C and U_A are defined as the mobilities of the cation and anion.]

The modern theory of the conductivity of electrolytes is due to Debye and Hückel, and is known as the Debye-Hückel theory.

There are several forces acting on an ion travelling through a solution. If we consider a single ion, say a sodium ion in a solution of common salt, it is surrounded by other ions. Now, the liquid as a whole is neutral; the positive ions exactly balance the negative ions. The positive sodium ion is surrounded by a small electric field which contains the balancing negative chloride ion and therefore has a slight preponderance of negative charge. The ions surrounding the sodium ion we are considering constitute the "ionic atmosphere" of that ion. The ions which form the atmosphere are in continual movement, so that the preponderance of negative charge is not concentrated in one place in the atmosphere but is distributed symmetrically about the central ion. Because the ions are in continual rapid motion, any dissymmetry in the atmosphere soon averages itself out so that the atmosphere can be treated as though it were always symmetrical. The effect of the ionic atmosphere decreases outwards from the central ion and very soon ceases to be measurable.

Every ion in the solution is surrounded in this way by an ionic atmosphere. In the solution of common salt, for instance, every chloride ion is at the centre of an atmosphere on which there is a slight preponderance of positive charge.

When a sodium ion advances through the solution, it moves away from the centre of its ionic atmosphere. The negative atmosphere exerts a small backward drag, which acts as a check on the forward movement of the (positive) ion. The atmosphere readjusts itself symmetrically about the new position of the ion, but this adjustment takes a little time (the "time of relaxation"); meanwhile the ion has moved a little farther on still, so the backward drag continues. The quantities are, of course, very small. The effective radius of the ionic atmosphere is about 10^{-7} cm.; the time of relaxation is about 10^{-10} seconds.

In addition to the retarding effect of the ionic atmosphere there are two other forces which retard the movement of ions through the solution. One of these is the usual viscous force which opposes motion through any liquid. The other is a force of a similar nature, due to the fact that—in an electric field—the positive ions move in the opposite direction to the negative ions. The opposite streams interfere with one another, and slow one another down.

Suppose, then, we place the solution in an external electric field. The ions will be attracted in one direction or the other, the positive ions towards the negative electrode and the negative ions towards the positive electrode. The attraction due to the external field is opposed by the three forces we have just been considering, and we have :

Force due to external field

$$= \text{Force due to the ionic atmosphere} + \text{Viscous drag due to the solvent} + \text{Viscous drag due to the movement of the ions in opposite directions.}$$

[The ion accelerates until the equilibrium represented by the equation above is set up ; thereafter it moves with constant velocity. Actually, the constant velocity is reached in an extremely short time.]

Two of the three opposing forces evidently depend on the concentration of the solution : the ionic atmosphere is more diffuse in a weaker solution, because the ions are farther apart ; so it exerts a smaller drag back on the forward motion of the ion. The second viscous force is smaller in a weaker solution because the opposite streams of ions are farther apart, and do not slow one another down to such an extent.

The older theory left out of consideration the two forces which depend on the concentration. According to this theory, therefore, the speed of the ions was not affected by changes in the concentration of the solute. Differences in the equivalent conductivity were ascribed solely to differences in the degree of ionisation of the solution. (It will be remembered that the equivalent conductivity depends both on the speed of the ions and on the degree of ionisation.)

The modern theory includes all three forces retarding an ion.

The older theory led to a certain relation between the equivalent conductivity and the concentration; this relation held quite accurately for such electrolytes as are but slightly ionised, but it broke down completely when applied to electrolytes that are strongly ionised, such as common salt. [This is the famous "anomaly of strong electrolytes."]

According to the Debye-Hückel theory, to get a relation between the equivalent conductivity and the concentration we must take into account changes both in the speed of the ions and in the degree of ionisation. If we neglect the latter effect and assume that the electrolyte is *completely* split up into ions throughout, we obtain the relation :

$$\Lambda_c = \Lambda_0 - K\sqrt{c}$$

Λ_0 is the conductivity at zero concentration (infinite dilution); Λ_c is the conductivity at concentration C ; and K is a constant (which can be calculated from the theory). Within the range where this equation holds, the equivalent conductivity is always less than that at infinite dilution—less by an amount proportional to the square root of the concentration.

This relation does hold quite accurately for dilute solutions of strong electrolytes (up to, say, a concentration of one in a thousand). It was, in fact, discovered empirically long before the Debye-Hückel theory was brought forward; it was used for many years for certain purposes. This can be taken both as an indication of the accuracy of the Debye-Hückel theory, and of the hypothesis that strong electrolytes are completely ionised in dilute solution. (There is, moreover, independent evidence for this latter hypothesis.)

The problem of concentrated solutions remains a difficult one. The law :

$$\Lambda_0 = \Lambda_c + K\sqrt{c}$$

breaks down. We do not know how far the deviations from this equation are due to the numerous approximations which Debye and Hückel had to introduce into their theory, and

how far they are due to incomplete ionisation in concentrated solutions.

The value of the theory is shown by certain predictions that have been made from it. Two important predictions have been made in the field of conductivity :

(1) When very high voltages are used, the ions move at very high speeds ; the ionic atmosphere has no time to form round them. There is, therefore, no drag back due to the ionic atmosphere ; nor does the second viscous force, due to the two streams of oppositely charged particles, have any effect. The speed of the ions should, therefore, be equal to the speed at infinite dilution. This has been confirmed experimentally.

(2) In a high-frequency alternating field, the ions should move to and fro with great rapidity (instead of steadily forward). The movement is so rapidly alternating and so short, that the ions never move far from the centre of the ionic atmosphere. Hence the drag back due to the ion moving from the centre of its ionic atmosphere never takes effect. But the ionic atmosphere is present, so the viscous drag due to the opposite movement of the oppositely charged ions is still present. Thus the speed of the ions should be greater at higher frequencies, because the drag back due to the ionic atmosphere is not present ; but it should not be so great as the speed at infinite dilution, because the second viscous force is still present. This also has been confirmed experimentally.

THE CONDUCTIVITY OF ACIDS.—Acids are substances which are capable of giving hydrogen ions. The hydrogen ion has an unusually high mobility in solution—some half dozen times as great as that of other ions. It might be thought that the small size of the hydrogen ion would account for its high velocity ; viscous forces are much less effective in retarding a small particle than a large one. But we now know that the hydrogen ion does not exist as such in solution at all. In water, for instance, it is hydrated to H_3O^+ and does not occur as H^+ ; in other solvents it is solvated in a similar way.

The small size of the ion is, therefore, untenable as an

explanation of the high speed of the ion. There has been a return to something like the old Grotthus chain theory of conductivity to account for the mobility of the hydrogen ion; this theory has, of course, been discarded in other cases.

The idea is that a hydrogen ion is passed on from one water molecule to another, in the way indicated in Fig. 78. In (1) the H_3O^+ ion is shown on the left, with water molecules to the right of it. In (2) a hydrogen ion has been transferred from the H_3O^+ ion to the nearest water molecule—this water molecule has now become an H_3O^+ ion. (3) shows a further stage in the process. A different

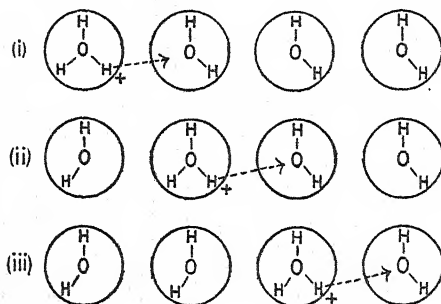


FIG. 78.—Conductivity of the hydrogen ion.

hydrogen atom is involved at each stage; it is as though the hydrogen ion were passed from molecule to molecule without actually traversing the distance between them.

The hydroxyl ion also has an abnormally high mobility, and a similar mechanism can be devised to explain this. In (1) the hydroxyl ion is shown on the left. A hydrogen ion from the nearest water molecule unites with this ion to form a water molecule; the ion is thus transferred one place to the right, and so the process goes on.

In Figs. 78 and 79 it will be seen that only one of the hydrogen atoms in each water molecule is involved in the chains; the other takes no part at all. Thus we might replace one of the hydrogen atoms of water by some other group, and such chains could still be formed. It is a strong

confirmation of the theory that the high mobility of the hydrogen ion occurs only in solvents containing the OH group—just the solvents in which such chains can be formed. Ordinary alcohol is such a solvent; its molecules are water molecules in which one of the hydrogen atoms has been replaced by the ethyl group, C_2H_5 ; its composition is C_2H_5OH . The hydrogen ion has the expected high mobility in this solvent. In ether $(C_2H_5)_2O$, both the hydrogen atoms of water have been replaced by C_2H_5 groups; the OH group is lacking and with it the high mobility of the

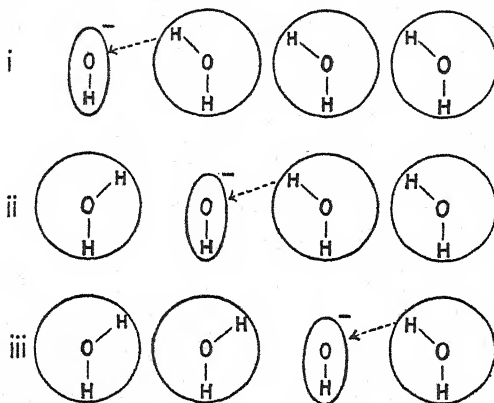
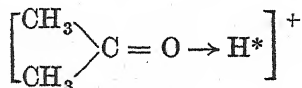


FIG. 79.—Conductivity of the hydroxyl ion.

hydrogen ion. Acetone, $CH_3.CO.CH_3$, and nitromethane, $CH_3.NO_2$, are further examples of liquids not containing the OH group. When acids are dissolved in these liquids the hydrogen ions do not have an abnormally high mobility. In acetone solution, for instance, the hydrogen ion yields the ion :



The most that can happen is for the hydrogen atom marked * to be given up again; there is no possibility of a hydrogen ion being given up in a different part of the molecule, so the essential condition for an abnormal mobility is lacking.

It is only to be expected that the addition of water will have some effect on the conductivity of acids dissolved in non-aqueous solvents ; but small quantities of water often have remarkably large effects.

Suppose we have a strong acid, an acid which is strongly ionised, dissolved in a solvent, like alcohol, which contains the OH group. If only one part in a thousand of water is added, there is a considerable effect. This small addition reduces the conductivity by as much as 20 per cent. The reason for this surprisingly large decrease is that the water molecules take up the hydrogen ions, giving H_3O^+ ions, and hold them much more firmly than the alcohol does. The water molecules do not readily pass on the hydrogen ions to alcohol molecules, so that a water molecule does not readily form part of a chain whose other members are alcohol molecules. If there were enough water to provide an alternative route for the ions, the result would be different ; but the small amount of water acts almost entirely as a check on the speed of the ions.

If a strong acid is dissolved in a solvent which does not contain the OH group, the result of adding a small amount of water is different. There is no question of "Grotthus chains" in this case, and the conductivity of the acid is hardly affected at all by the addition of water.

The effect on weak acids, and weak electrolytes generally, is surprisingly different. Whether the solvent contains an OH group or not, the addition of one part in a thousand of water has the effect of increasing, not decreasing, the conductivity ; the increase may be as much as 50 per cent. This extraordinary increase in conductivity is due to a great increase in ionisation. Water is the best ionising solvent known ; it increases the ionisation of the weak electrolyte, and hence increases its conductivity.

CHAPTER XXIV

TRANSPORT NUMBERS

A SOLUTION of an electrolyte will, as we know, conduct electricity. The current flowing through such a solution consists of two streams of ions: a stream of positive ions toward the negative electrode (the cathode) and a stream of negative ions toward the positive electrode (the anode). In a solution of common salt, for example, the sodium ions carry a positive current toward the cathode, and the chloride ions carry a negative current toward the anode. A positive current in one direction is equivalent to a negative current in the opposite direction; so the total current is equal to the arithmetical sum of the positive and negative currents.

In a solution of common salt, the sodium and chloride ions do not carry equal currents—the chloride ions actually carry more current than the sodium ions. Now there are just as many sodium ions as chloride ions, and the sodium ion has a charge of the same size as the chloride ion (although the signs of the charges are, of course, opposite). The reason why the chloride ions carry more of the current than the sodium ions must, therefore, be because they move more rapidly—in other words, because they have a greater mobility.

The fraction of the total current which is carried by an ion is called the transport number of that ion. The sum of the transport numbers is unity, for the two ions together carry the whole current. The transport number of any ion is proportional to its mobility. (If the mobility of one ion is double that of the other ion, obviously it carries twice as much current as the other, and its transport number is twice as great. Since the sum must be unity, the transport numbers in this case would be $\frac{2}{3}$ and $\frac{1}{3}$.) Hence it arises

that if we find the ratio of the transport numbers we have also found the ratio of the mobilities of the ions.

The conductivity of a solution is equal to the sum of the mobilities of the ions ; in effect, it is the sum of the rates at which the ions carry charges in one direction or the other. If we can measure the transport numbers of the ions, we shall then know both the sum of the mobilities and their ratio ; so we shall be able to calculate the separate mobilities of the ions. If x and y are the mobilities of the two ions in a solution, then :

$$x + y = c$$

where c is the equivalent conductivity of that solution. If the measured ratio of the transport numbers is t , then :

$$\frac{x}{y} = t$$

Hence, by elementary algebra :

$$x = \frac{ct}{1+t} ; y = \frac{c}{1+t}$$

It is therefore important to be able to measure the transport numbers of ions. The classical method of doing this is due to Hittorf. His method depends on the following considerations. Suppose a substance AB, which consists of ions A^+ and B^- , is being electrolysed. As the electrolysis proceeds there is less and less of the electrolyte in solution. Care is taken not to disturb the liquid in the central portion of the cell, by stirring or otherwise. Then nearly all the loss of electrolyte is from the parts of the solution round the electrodes ; the liquid in the middle is as concentrated as ever.

We can imagine that the electrolytic cell is divided into three compartments, as shown in Fig. 80 ; there is, of course, no actual physical barrier between the three parts of the cell. It is arranged that there shall be no loss of electrolyte from the central compartment ; when the method is being used practically, the solution in the central part of the cell is analysed before and after the experiment, to ensure that there really is no change in composition there.

The A^+ ion is discharged at the cathode. If U is the mobility of this ion, then a quantity of A^+ proportional to U is moving across to the cathode every second. For convenience, we will suppose that the size of the cell is so chosen that the quantity of A^+ is *equal* to U . Then, as regards the central compartment, a quantity equal to U is entering every second, and the same quantity is leaving on the other side of the compartment; hence there is no net change in the central compartment. Simultaneously, quantities of the B^- ion, equal to V , its mobility, are crossing in the opposite direction. Once again there is no change in the middle compartment.

Now let us see what is happening in the cathode compartment. Every second a quantity of A^+ , equal to U , enters, and a quantity of B^- , equal to V , leaves, the compartment. This would represent a net gain proportional to $U - (-V)$ or $U + V$ positive charges; therefore $U + V$ is the amount of the A^+ ion discharged per second at the cathode.

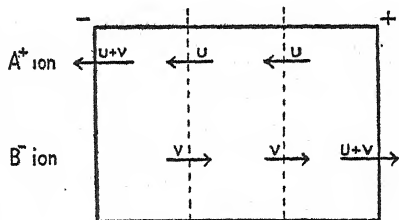


FIG. 80.

At the same time the anode compartment gains V negative charges and loses U positive charges, so that $V - (-U)$ or $V + U$ negative charges are discharged per second at the anode.

In all, then, $U + V$ molecules of AB are lost: $U + V$ ions of A^+ at the cathode and $U + V$ ions of B^- at the anode. This loss occurs from the cathode and anode compartments, but it is unequally distributed between them. In the cathode compartment there is a net loss of V units of AB ; for U units of A^+ enter the compartment and $U + V$ are discharged, and V units of B^- leave the compartment (a net loss of V units of each ion). Similarly, there is a net loss of U units of AB from the anode compartment.

If we measure how much electrolyte is lost by the cathode

and anode compartments, we can find the ratio of U to V , for :

$$\frac{\text{Loss of electrolyte at anode}}{\text{Loss of electrolyte at cathode}} = \frac{U}{V}$$

This does, in fact, give us the ratio of the mobilities, or, what is the same thing, the ratio of the transport numbers.

Suppose in a particular case that the ratio $\frac{U}{V}$ is equal to k .

Then :

$$\frac{T_A}{T_B} = k$$

(T_A and T_B are the two transport numbers.)

But :

$$T_A + T_B = 1$$

So, by simple algebra,

$$T_A = \frac{k}{k+1}; T_B = \frac{1}{k+1}$$

THE MOVING BOUNDARY METHOD. — An extremely interesting way of measuring transport numbers—the “moving boundary” method—has been perfected by MacInnes.

Fig. 81 shows the principle of the method. The solution to be investigated is placed in the lower part of the long narrow U-tube ; in the diagram it is supposed that a solution of common salt, NaCl , is being examined. A solution of lithium chloride, LiCl , is placed above the sodium chloride in one limb of the tube, and a solution of sodium acetate, NaAc , is used to fill up the other limb. (Ac is a convenient contraction for the acetate ion, $\text{C}_2\text{H}_3\text{O}_2$.)

It is arranged that there is a sharp boundary at A and B between the two layers. MacInnes used the following device to obtain sharp boundaries in each case : the solutions were contained in tubes, each with a small glass plate on the end. The lower tube was filled until a drop of solution projected from it, and a drop was also allowed to hang from the upper tube. When the two plates were made to slide

across one another, the projecting drops were sheared off and a sharp boundary between the two solutions was obtained at the point where the tubes met.

The principle of the method is to observe the rate of movement of these boundaries when an electric current is passed through the solutions in the apparatus. For this purpose electrodes are introduced into the two ends of the U-tube. [Reversible electrodes must be used, since we are using direct current; if we used irreversible electrodes, polarisation would set in to a troublesome extent.] The positive electrode is in the lithium chloride solution, and the negative electrode in the sodium acetate solution.

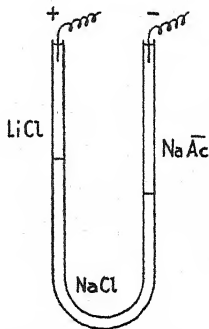


FIG. 81.

When an electric current is passed through the U-tube, the Li^+ and the Na^+ ions begin to move away from the anode, the positive electrode; they begin to move down the left-hand tube. Thus the boundary between the two solutions moves down the tube. The negative chloride ions, Cl^- , meanwhile, move up the left-hand tube toward the anode; but this does not affect matters; there are chloride ions on both sides of the boundary. In the right-hand limb the negative ions, the acetate and chloride ions, Ac^- and Cl^- , move down the tube, and again the boundary moves slowly downward.

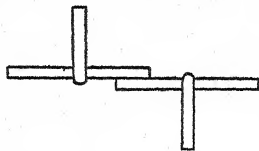


FIG. 82.—Method of obtaining sharp boundaries.

Here there are Na^+ ions on both sides of the boundary, and their motion up the tube makes no difference to the motion of the boundary.

It is easy to measure how fast the boundaries move. The position of the boundary at any moment can be seen by eye, particularly if the illumination is suitably arranged. So it is only necessary to place a scale behind the tube and time the movement of the boundary against this scale. It

is usually arranged that the boundary shall travel about an inch in five minutes.

The rate of movement of the left-hand boundary depends on the speed of the sodium ions; if the sodium chloride is completely ionised, the speed of the boundary is indeed equal to the speed of the sodium ions. Similarly, the rate of movement of the right-hand boundary depends on the speed of the chloride ions. Hence the ratio of the rates at which the boundaries move is equal to the ratio of the speeds of the ions, and thus to the ratio of the transport numbers.

There are several interesting points about this method. The reason for the choice of the upper solutions is easy to see: that on the left-hand side (the anode side) must contain the same negative ion as the solution being tested; in our case, both solutions contain the chloride ion. Similarly, on the right-hand side (the cathode side) both solutions must contain the same positive ion; in our case, the sodium ion.

The second ion in each of the upper solutions is chosen so that its mobility is less than that of the ion being tested. Thus the lithium ion is placed above the sodium ion, because it has a lower mobility than the sodium ion; similarly, the acetate ion has a lower mobility than the chloride ion. But the ions in the upper solution must not "get left behind" by the ions in the lower solution, although they have a lower mobility. For this reason the upper solutions are made more dilute than the solution being tested; if they are just dilute enough the lithium ions will move at the same speed as the sodium ions they follow, and the acetate ions will move as fast as the chloride ions.

The reason for this is that the electrical resistance of a solution becomes greater as we dilute it; there are fewer ions present to carry the current. But the current must be the same in all parts of the apparatus, so the ions in the weaker solution must travel faster to make up for their smaller number. If the concentrations are just right, the lithium ions will travel at the same rate as the sodium ions, and the acetate ions at the same rate as the chloride ions.

[The potential gradient is greater in the lithium chloride solution than in the sodium chloride solution ; it is greater in the solution of high resistance. This greater potential gradient makes up for the lower mobility of the lithium ions.]

But to get the concentrations just right it would be necessary to know beforehand the mobilities of the ions concerned : we should have to know beforehand what we set out to measure. Fortunately, this is not necessary. If we get the adjustment of the concentrations nearly right, the solutions will themselves make the final adjustment. Suppose the lithium chloride is too concentrated. There are too many ions present, so they do not move so quickly as they would if the solution were correctly adjusted. The lithium ions lag behind the sodium ions, so that the lithium chloride solution becomes weaker until the lithium ions are moving at just the same rate as the sodium ions. If, on the other hand, the lithium chloride solution is too weak, then the lithium ions travel too fast and accumulate at the boundary ; they accumulate until the right adjustment of the concentration of the lithium chloride solution has been made. Just the same sort of thing occurs at the chloride-acetate boundary.

Perhaps the most interesting point is that sharp boundaries between the solutions should persist at all : why do they not fade away on account of diffusion ? We have just seen that the lithium chloride solution is weaker than the sodium chloride solution, in order that the lithium and the sodium ions may travel at the same speed. Suppose a particular lithium ion happens to travel a bit faster than the average ; it may actually manage to get into the sodium chloride solution ahead of it. But here it meets a more concentrated solution than the one it has just been in, and, as we know, ions travel slower in more concentrated solutions ; the speed of the lithium ion is, therefore, checked immediately it enters the sodium chloride solution. [The lithium ion moves more slowly in the sodium chloride solution because there is a smaller potential gradient there than in the lithium chloride solution. This effect must not be confused with

that discussed in the previous chapter, namely, that an ion has a smaller mobility in a concentrated than in a dilute solution. Mobilities, it will be remembered, are referred back to a *constant* potential gradient.] Thus, any lithium ion which happens to diffuse into the sodium chloride solution will fall behind until the boundary catches it up again and it is once more back in the lithium chloride solution. Similarly, any sodium ion which happens to diffuse into the lithium chloride solution is speeded up until it returns across the boundary again. Neither ion, therefore, moves much beyond the boundary, and the sharpness of the boundary is preserved.

If potassium permanganate is used as one of the solutions, any diffusion taking place is easy to observe because permanganate is coloured. So long as there is no current running, the permanganate can be seen to diffuse into the solution above it. As soon as the current is started, diffusion ceases and the boundary begins to get sharper—for the reason described in the last paragraph; soon there is a sharp division between the two solutions.

[There are other methods of measuring transport numbers; the E.M.F. method is interesting as it is the only method which has been applied to solutions in liquids other than water, *e.g.*, solutions in methyl alcohol.]

CHAPTER XXV

COLLOIDAL SOLUTIONS

MOST of the ordinary things of life are colloidal. We feed ourselves almost entirely on colloids; milk and tea are colloidal; we clothe ourselves in colloids; such everyday things as leather, wood, starch, glue, gelatin, albumen, and soap are colloidal.

But it is not easy to give an exact definition of a colloid. There is the same sort of difficulty as there is in defining what we mean by a metal. The extreme cases are clear enough—iron, copper, gold, etc., are obviously metallic—but near the borderline there are doubtful cases, elements possessing some of the properties of metals but lacking others, so that we do not know whether to classify them as metals or non-metals. It is just as difficult to make a rigorous distinction between colloids and non-colloids.

In this chapter we shall be speaking of colloidal solutions rather than of colloids in general; it is convenient to use the term “sol” in place of the longer “colloidal solution.” We must also introduce the terms “disperse phase” and “dispersion medium.” The disperse phase is the substance which is broken up into fine particles in a solution or suspension; it is the substance dissolved or suspended. The dispersion medium is the substance, usually a liquid, in which the dispersion occurs. (In the case of ordinary solutions, the solute is the disperse phase, and the solvent is the dispersion medium.)

The distinction between an ordinary solution and a colloidal solution lies in the size of the particles of the disperse phase. In an ordinary solution the particles are of molecular size; the molecules of the solute are separate and each is surrounded by the dispersion medium. In a colloidal solution the particles are larger; the molecules

are in little groups called "micelles." If the particles are larger still we get a suspension.

A colloidal solution is, therefore, an intermediate stage between an ordinary solution and a suspension. There are no sharp limits between the three classes. There are, however, distinctive properties which make their appearance when the particles reach a certain size and which fade out when the particles are larger. For this reason solutions containing particles of intermediate size are classed together as colloidal solutions.

If the molecules of a substance are small it will probably give ordinary solutions rather than colloidal solutions. Some molecules, such as those of gelatin, are probably of colloidal size themselves; so that even if the molecules of such a substance are separate in solution, nevertheless the solution will be a colloidal one.

A filter paper gives a rough means of distinguishing between a colloidal solution and a suspension. The particles in the sol are small enough to pass through the pores of the filter paper, whereas the particles of the suspension are too large to pass through. At the other end of the scale, colloidal solutions may be distinguished from ordinary solutions by means of a filter of parchment paper. The disperse phase in an ordinary solution passes through the minute pores of the parchment paper, but the larger particles of a colloidal solution cannot do so. This method of distinguishing between ordinary solutions, sols, and suspensions works quite well in practice; it is not so crude as it sounds.

The particles in a sol are bigger than those in an ordinary solution, but they are still so small that it is impossible to examine them even by means of the highest-power microscope. The ultra-microscope, however, provides a way. In this instrument a beam of light is thrown on to the sol. The sol is then examined through a high-power microscope placed at right angles to the beam of light. The particles of the sol are large enough to scatter in all directions the light falling on them, so they appear in the microscope as moving points of light (like motes in a sunbeam). The particles can be seen to be in continual movement; they

move in an irregular zig-zag path, at all sorts of angles, rather like the movements of water-fleas in pond water. This jerky motion of the particles is called the Brownian movement.

The particles in a sol are at just about the limit of size that enables them to scatter light falling on them. It is not surprising, then, to find that some of them scatter light of certain frequencies (colours) to a greater extent than they scatter light of other frequencies. This is why sols are often coloured. The colour of the sol must depend on the size and shape of the particles dispersed in it; so the colour of a sol may differ according to the way it has been prepared.

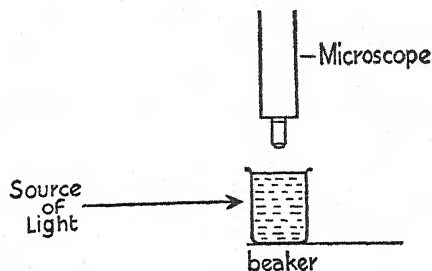


FIG. 83.—Arrangement of the parts in the ultra-microscope.

Thus gold sols may be red in colour, or they may be orange, or blue, or violet.

This classification according to the size of the particles, into ordinary solutions, sols, and suspensions, replaces the older classification of substances into "colloids" and "crystalloids." The old classification attempted to divide *substances* into two classes; we now prefer to consider different states of division of the disperse phase instead. This is justified when we realise that most of the so-called crystalloids will, in suitable conditions, yield colloidal solutions.

The most obvious way of compelling a substance to form a sol is to grind it to an exceedingly fine powder, that is, to a powder in which the particles are of colloidal size. This can actually be carried out. The substance is ground

as finely as possible by ordinary methods, and is then made into a suspension by shaking it up with a liquid. The suspension is passed between two rapidly revolving metal discs; the discs are very close together and they rotate in opposite directions. This reduces the suspension to a sol, simply by grinding the particles till they are of colloidal size. (The revolving discs used in this way are known as a "colloid mill".)

A quite different way of reducing a substance to particles of colloidal size was devised by Bredig; it is used to prepare colloidal solutions of metals. Two electrodes of the metal in question are placed in conductivity water. (This is the purest water made; it is used in experiments on the electrical conductivity of solutions.) A powerful oscillatory current is used to send sparks across the gap between the electrodes. During the sparking, fragments of metal of colloidal size are broken off from the electrodes; these fragments are dispersed throughout the water, and so form a colloidal solution of the metal. The method has been extended to other liquids than water: ether, for instance, has been used as the dispersion medium in making colloidal solutions of metals which react with water—sodium, for example.

In both these methods of making sols we start with the substance in bulk and break it up into particles of colloidal size. We can also start at the other end, with an ordinary solution; here the particles are smaller than colloid particles, and it is necessary to get them to aggregate together into micelles. As an example of this method: a solution of chlorplatinic acid, H_2PtCl_6 , is made; this is an ordinary solution, the molecules are separate. Formaldehyde is added to the solution; it reacts with the chlorplatinic acid, and sets free atoms of platinum. These atoms of platinum then aggregate into particles of colloidal size. This method is not successful in every case; often the atoms set free initially aggregate to form particles which are larger than colloid particles, and the result is a suspension or a precipitate.

Probably all substances can be made into colloidal

solutions, but not all with equal ease. There is one class of substances which can be made into colloidal solutions very easily; they are called hydrophilic (that is, water-loving) colloids. Gelatin is a hydrophilic colloid. It has only to be warmed with water to persuade it to form a sol; it breaks up at once into particles of colloidal size.

The other class of substances—gold may be taken as an example—are called hydrophobic (water-hating). It is only with some difficulty and by the use of special devices that they can be got into colloidal solution. A few of these devices have been mentioned already, the use of the colloid mill, Bredig's method, etc.

The classification into hydrophilic and hydrophobic colloids—like most of the classifications of colloid chemistry—is not a sharp one. There is every shade of gradation from one extreme to the other.

The particles in a sol are electrically charged. In some sols the particles are positively charged and in others they are negatively charged. Of course, the sol as a whole is electrically neutral; there are charges on the ions in the dispersion medium, balancing the charges on the particles of the disperse phase.

The existence of these charges on the particles in a sol can be demonstrated by placing the sol in an electric field. The attraction of positive electricity for negative draws the charged colloid particles toward one electrode or the other. If the particles are charged positively they are drawn toward the negative electrode (the cathode); if they are charged negatively they are drawn toward the positive electrode (the anode). [This process is called "cataphoresis."] In this way it has been shown that colloidal gold and silver are usually charged negatively; aluminium hydroxide and ferric hydroxide are usually charged positively; and so on.

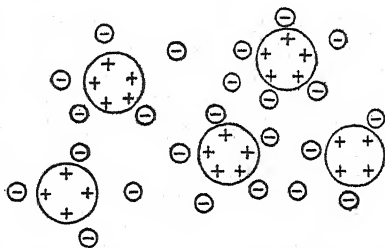


FIG. 84.—The charges on the particles of a positively charged sol.

When the charged particles reach the electrode towards which they are moving, they are neutralised; they lose their charges. The sol coagulates in the neighbourhood of the electrode. This shows that the stability of a sol is conditioned by the charges on the particles of the disperse phase. So long as the particles are charged their mutual repulsions keep them apart and prevent their aggregating together and eventually precipitating. When the charges are removed in any way, the particles aggregate together and the sol coagulates.

It is natural to enquire where the charges on the particles in a sol come from. It is probable that the origin of these charges is not the same in every case. Often, no doubt, the micelles adsorb ions from the solution and so acquire a charge; this is supported by the fact that, although larger quantities of electrolytes coagulate colloids, yet it is often necessary that small quantities of electrolytes shall be present in the solution before a sol can form at all. Even if no electrolyte is present in the solution, yet it must be remembered that water itself is feebly ionised, giving hydrogen and hydroxyl ions; one or other of these ions may be adsorbed by the micelles. In some cases it is probable that the charges originate by the ionisation of the micelles themselves. The particles in a silicic acid sol, for example, consist of silicic acid, and this might quite well ionise; (positive) hydrogen ions would be lost, leaving the micelles with a negative charge.

If, say, positive ions are adsorbed by the micelles in the sol, then there must be balancing negative ions throughout the solution. The positively charged micelles will attract the negatively charged ions in the solution, so there will be a tendency for these negative ions to arrange themselves round the micelles. In this way an electric double layer is formed: a layer of positive charges in close proximity to a layer of negative charges. The layer is not absolutely "rigid": the negative ions do sometimes leave it and wander off through the solution. (Fig. 84.)

Sols of hydrophobic colloids are particularly easy to coagulate; the addition of a small quantity of an electrolyte

is sufficient to bring this about. The electrolyte is ionised ; the ions have charges of opposite sign, so one of them must have a charge opposite to that of the particles of the sol. The charge on the sol is neutralised by the opposite charge on this ion, and the particles are no longer mutually repelled ; they form larger particles, which fall as a precipitate.

A gold sol may be coagulated in this way by adding an aluminium salt to it. The particles of the gold sol are negatively charged ; the aluminium ion has three positive charges. The aluminium ions, therefore, tend to neutralise the charges on the micelles of gold. If only a little aluminium salt is added, the charges on the micelles will be decreased, but not completely neutralised. This can be demonstrated by seeing how fast they move in an electric field ; the bigger the charges, the faster the movement. The first small addition of aluminium salt reduces the speed considerably. If more is added, the gold micelles are neutralised completely, and the sol precipitates. If a still larger amount of aluminium salt is added it is possible to give the micelles a positive charge ; the sol is thus stable again and does not coagulate. The particles in the sol now move toward the cathode instead of the anode.

An aluminium salt is particularly good for precipitating negative colloids. An ion with a high charge always has a much greater effect than an ion with a small charge. The aluminium ion, with a charge of three units, is a thousand times as effective as the sodium ion, with a charge of only one unit. This explains why alum is used to precipitate objectionable colloidal matter in swimming baths and also in sewage.

The rapid coagulation of hydrophobic colloids is sometimes a disadvantage ; this is the case, for example, with colloidal solutions used in medicine. Fortunately it is possible to "protect" hydrophobic colloids against coagulation. We can do this by adding to the sol an excess of a hydrophilic colloid such as gelatin. There is, of course, no need to protect hydrophilic colloids themselves ; a solution of starch, for example, will persist indefinitely. Colloidal silver is a sol which has some value in medicine, both for

injections and as an ointment ; its value depends on the very small size of colloid particles. It would be of little use if it were to coagulate quickly ; so a hydrophilic colloid is added to protect the silver sol. The protective colloid has another effect, too : it enables us to obtain colloidal solutions of hydrophobic colloids at a much greater concentration than is possible in their absence.

CHAPTER XXVI

GELS, EMULSIONS, AND FOAMS

GELS.—Ordinary jelly is an example of what the chemist calls a gel (with a soft g). As is often the case in colloid chemistry, it is difficult to say exactly what is meant by a gel, although it is generally easy enough to recognise one when you meet one. Gels are usually transparent or semi-transparent, and they often have a typical "wobble" due to their peculiar elastic properties.

Beyond that it is difficult to go until we bring the ultra-microscope to our aid. This instrument reveals that gels, like colloidal solutions, are not absolutely homogeneous. Gels contain both a liquid and a solid, interweaving with one another in a very close structure. The liquid and the solid in the gel form separate phases, so we will speak of the "liquid phase" and of the "solid phase." We cannot see the structure of a gel in the ordinary way because it is on such a small scale, as small as the scale of colloid particles. (It has recently been suggested that in some cases the liquid phase may be glass-like.)

It is, however, fairly easy to make it clear that gels are not homogeneous, that they do possess some sort of structure. We can do this by producing small bubbles of gas in the middle of the gel. The bubbles are not spherical, as they would be if they were produced in an ordinary liquid, but they are lenticular in shape; the structure of the gel distorts them. (Such bubbles may be produced by impregnating the gel with a little sodium carbonate, and then allowing acetic acid to diffuse into it; bubbles of carbon dioxide are produced in the gel.)

The solid phase in a gel consists of a mass of minute threads interlacing one another. These threads, or "fibrils," are very thin; they are usually flexible, and often crystalline.

Sometimes the fibrils are simply long molecules, such as stearic acid molecules. Sometimes they consist of long chains of separate molecules.

All gels have a certain amount of rigidity. It is the solid phase that gives the gel its rigidity. Some gels, however, possess the familiar jelly wobble, whilst others do not. The former are called elastic gels, and the latter are called rigid gels. The difference between the two classes of gels is a difference in the kind of fibrils: if the fibrils are flexible and yield easily, then we have an elastic gel; if the fibrils are rigid, the gel is rigid too.

The liquid phase in a gel is continuous. This is easily shown because substances soluble in the liquid will readily diffuse through the gel. For instance, if we make a gelatin gel and pour copper sulphate on top of it, the blue colour of the copper sulphate soon penetrates down into the gel.

The substance which diffuses through the gel should be dissolved in the same liquid as the liquid phase of the gel. The separate molecules can then pass through the liquid phase without being seriously impeded by the network of solid fibrils; the molecules move nearly as rapidly through the gel as they do through the pure liquid. Particles of greater size than molecules will not diffuse through the gel; a substance in colloidal solution, for example, will not diffuse through it. Still less will macroscopic objects pass through it—not, at any rate, without breaking up the gel.

The liquid phase in a gel is partly adsorbed on the solid fibrils, and partly simply enmeshed in the network of fibrils. There are several phenomena which afford evidence of this. Bachmann observed the setting of a gel under the ultra-microscope. As the cooling of the sol went on, the light scattered by the particles in it became brighter and brighter; this shows that the particles in the sol increase in size during the cooling. This can only mean that the particles are adsorbing the liquid on their surfaces. Bachmann observed also that the Brownian movements, the irregular jerky motion, of the particles became more and more sluggish and finally ceased altogether when the sol had set to a gel.

Gels exude water if they are allowed to stand. The gel

shrinks and drops of water appear on its surface. This phenomenon is called syneresis. It is due to the fibrils attracting one another and squeezing out the water enmeshed in the gel. Syneresis is greater in concentrated than in dilute gels, and often increases as time proceeds because the gel is steadily becoming more concentrated. This may seem surprising—the water is exuded most rapidly from the gels which contain the least. The reason is that the fibrils are closer together in the more concentrated gels; they attract one another more strongly so that the water is exuded more rapidly than in dilute gels.

Throughout the shrinkage (except, perhaps, in the final stages) the total volume of the gel and the water exuded remains the same. This indicates that it is only the water accidentally enmeshed in the gel that is exuded. To remove the water adsorbed on the fibrils it is necessary to use more drastic methods in the form of chemical drying agents, such as sulphuric acid. Under such treatment elastic gels collapse; the framework of fibrils is not strong enough to maintain the structure. Rigid gels, however, maintain their shape; the framework of fibrils remains in position.

After dehydration the rigid gel has a strong chemical affinity for water. The drying process has removed the water from the surface of the fibrils, and the fibrils are very ready to take up that water again. The large area of the fibrils, due to the porous, open structure of the dehydrated gel, favours this rehydration.

Such dehydrated gels will take up other liquids besides water. For this reason silica gel—which is a rigid gel—finds considerable application industrially. It is used to collect organic vapours from gases containing them in small quantities. The silica gel adsorbs the vapours, and these are then readily recovered by heating the gel. The method is simpler and less expensive than the older method of condensing the vapours.

If a gel is placed in water it absorbs water and swells out. An extraordinary thing is that the volume of the swollen gel is less than the total volume of the original gel *plus* the water absorbed. Either the gel fibrils or the water absorbed

has become compressed during the process, probably the latter. This contraction is an indication that the water is adsorbed on the gel fibrils, not merely caught in the mesh of the gel. Familiar examples of the swelling of gels are seen in the swelling of wood and of rice grains when they are placed in water. The process is easily reversed; if exposed to the air the swollen wood or rice dries up and resumes its previous size.

The pressure of a gel during swelling is unexpectedly great. An experiment with discs of dried seaweed showed that at first this pressure was about fifty atmospheres—a third of a ton to the square inch! This enormous pressure accounts for some of the vagaries of growing things. The growing and expanding branch of a tree, for example, will crack and destroy a wall. The pressure is easily sufficient to account for the height to which sap rises in tall trees.

EMULSIONS.—Cod-liver oil emulsion, with its familiar exhortation to “shake the bottle before using,” is a typical emulsion. Emulsions are like colloidal solutions, except that the disperse phase and the dispersion medium are both liquids. (In a colloidal solution, the disperse phase is solid.) On the whole, however, the particles of the disperse phase in an emulsion tend to be larger than those in a colloidal solution. There is on record an emulsion in which the disperse phase consisted of drops 3 mm. across. This was not a merely temporary state of affairs: the drops always returned to this size after being broken up by shaking.

It is not every pair of liquids that will form an emulsion. For one thing the liquids must be incapable of mixing: if they can mix they will simply form an ordinary solution; as, for example, when water and alcohol are shaken up together. If the two liquids do not mix they will ordinarily form two layers, one on top of the other; water and oil behave like this. If the two layers are shaken up together vigorously, they form an emulsion; one of the liquids is broken up into small drops by the mechanical agitation, and dispersed throughout the other liquid. Such an emulsion will probably be unstable; when it is left standing the

two liquids begin to sort themselves out and soon separate into two distinct layers again.

To obtain a stable emulsion we must introduce some third substance. This third substance is called an emulsifying agent or an emulsifier. The emulsifying agent tends to go to the interface between the two liquids, to form a thin film round the droplets of the disperse phase. This has two effects. (1) If two droplets in the emulsion collide, the film of the emulsifying agent will hinder their coalescing; if they coalesced, they would have to break through the film. Thus the droplets remain small in size, and the emulsion is stable. (2) The film lowers the surface tension between the two liquids; it lowers the energy in the interface between them. Now the area of the interface is enormously increased during emulsification; the total surface area of all the little droplets is much greater than the area of the interface when there are two separate layers. The increase in area involves an increase in energy, because the interface always contains energy—as is made manifest by the existence of surface tension. If the surface tension is low, the increase in energy is low; if the surface tension is high, the increase in energy is high. Thus the increase in energy during emulsification is less in presence of the emulsifying agent, because the emulsifying agent lowers the surface tension. Hence the emulsifying agent exerts a stabilising influence on the emulsion.

Soaps are examples of good emulsifiers; with their aid we can obtain stable emulsions of oil in water. It is possible also to use a solid as an emulsifying agent. Lampblack, for instance, can be used in making an emulsion of water in benzene. (When we speak of an emulsion of water in benzene, we mean that the water is the disperse phase and the benzene the dispersion medium; the water forms separate droplets in a continuous film of benzene.) The small particles of lampblack are large enough to be seen under a powerful microscope; we can actually see the black particles of lampblack round the droplets of water in the emulsion.

The reason why lampblack acts as an emulsifier is that it

does tend to accumulate in the interface between the water and the benzene. If the drops of water in the emulsion were to coalesce, the area of the interface would decrease. This would mean that the lampblack particles would become more crowded; some of them would have to be forced out of the interface. Since this is contrary to the natural tendency of the lampblack to accumulate there, the drops of water do not tend to coalesce; the emulsion is stable.

In the emulsions we have been considering the disperse phase constitutes a considerable proportion of the emulsion—the emulsions are quite concentrated. The disperse phase may, indeed, make up as much as 99 per cent. of the whole emulsion. An emulsion of paraffin in water, using soap as the emulsifying agent, can be obtained as concentrated as this.

In such an emulsion the paraffin consists of separate drops with a thin, but continuous, film of water between them. This makes the emulsion fairly rigid, rigid enough to be cut into cubes with a knife. The drops of paraffin in the emulsion cannot be spherical, owing to the tight packing. Seventy-four per cent. of the disperse phase is the limit which permits of equal-sized spherical drops in an emulsion, whereas the emulsion in question contains 99 per cent. So the drops are more or less deformed from the spherical shape. Any attempt to deform the drops further is resisted, and it is this resistance that gives the emulsion a certain amount of rigidity.

It might be thought that with such a small percentage of water—only 1 per cent.—there might be some doubt that the water really was the dispersion medium, that the water and not the paraffin formed the continuous phase. Actually there are several ways of telling which is the dispersion medium.

In the case in question the water conducts electricity, but the paraffin does not. (The conductivity of the water is due mainly to the presence of accidental traces of electrolytes.) If therefore the emulsion conducts electricity, we know that it is the water which is the continuous phase,

because there is a continuous path for electric current ; if it does not conduct, then the paraffin is the continuous phase.

Another method is to see what happens when we add first water and then paraffin to the emulsion. It is easy enough to add liquid to the continuous dispersion medium ; whereas it is difficult to add any to the drops of the disperse phase, because each is a separate entity. If, therefore, the emulsion mixes readily with water, then it is very likely that water is the dispersion medium ; if it mixes readily with paraffin, then paraffin is probably the dispersion medium.

A still further method is to add a suitable dye to the emulsion. If the dye is soluble in the dispersion medium, it will spread readily through the emulsion ; but it cannot spread easily through the separate drops of the disperse phase. A water-soluble dye is added to the emulsion ; if water is the dispersion medium, the dye will stain it ; if paraffin is the dispersion medium, the dye will not stain it.

Of course, these methods are readily extended to emulsions of other liquids than water and paraffin.

Which liquid forms the dispersion medium and which the disperse phase depends in many cases on the emulsifying agent used. If we shake up oil with water, we may get either an oil-in-water or a water-in-oil emulsion. When sodium oleate is used as the emulsifier, an emulsion of oil in water is produced ; but if magnesium oleate is used as the emulsifier, the water is dispersed throughout the oil. Now, suppose we start with an emulsion of oil in water. What will happen if we stir in magnesium oleate ? At a certain point the magnesium oleate just cancels out the effect of the sodium oleate ; neither kind of emulsion is stable, and separate layers of oil and water appear. With a still further addition of magnesium oleate there is a " phase inversion," the water becomes the disperse phase and the emulsion is one of water in oil.

Similar things happen when we use solid emulsifiers. Lampblack emulsifies water in kerosene, but finely divided silica emulsifies kerosene in water. If we mix together lampblack and silica in certain proportions, it is impossible to obtain an emulsion at all, just as it is impossible to use

a certain mixture of sodium and magnesium oleate as an emulsifier.

It is known that lampblack is more easily wetted by oil than by water, whereas silica is more easily wetted by water than by oil. It has been suggested that this gives the clue to the difference in behaviour between these two emulsifiers. In an oil-in-water emulsion—produced by the action of silica—the interface between the silica and the water is greater in area than that between the silica and the oil. This is what we should expect: the larger surface is the one more easily wetted. For a similar reason lampblack gives a water-in-oil emulsion. This theory has been extended to

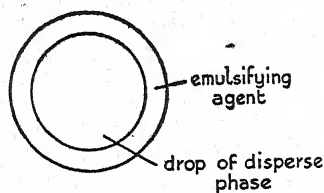


FIG. 85.—The outer surface of the emulsifying agent is greater than the inner surface.

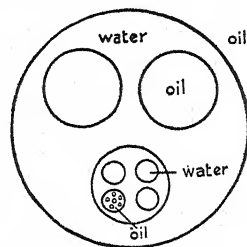


FIG. 86.—A multiple emulsion with five phases one inside another.

cover emulsifying agents in general, but it is doubtful whether it is quantitatively adequate.

The emulsions so far mentioned have been simple emulsions—simply drops of one liquid dispersed throughout another liquid. There are also multiple emulsions. In these emulsions each droplet of the disperse phase is itself an emulsion, containing still smaller droplets of another disperse phase. Such emulsions are often produced when a simple emulsion is shaken up with a suitable liquid. As many as five phases, one inside another, have been obtained. First there was a continuous phase of oil. This contained drops of water dispersed in it; each drop of water contained smaller drops of oil; these again contained drops of water; and finally these minute water drops contained even more minute drops of oil. There were thus alternately: oil, water, oil, water, oil.

Milk is one of the most important emulsions we meet with. It is an emulsion of fat in water, casein and lact-albumin being the emulsifying agents; of course, there are other things present as well, some sugars for example. It is not a very stable emulsion, for the fat soon rises to the top as cream. The cream carries with it some water, casein, etc., from the milk below, so it is still an emulsion.

In churning milk or cream to make butter, the essential thing to be done is to cause the fat which is dispersed throughout the emulsion to coalesce. The churning causes the milk or cream to froth, so that the water-air interface is enormously increased in area. Now the emulsifiers tend to go to the water-air interface rather than the water-fat interface; so during the churning the emulsifiers are removed from the water-fat interface. This removes the essential condition for the stability of the emulsion; the fat globules coagulate and form butter. The butter formed is, as a matter of fact, itself an emulsion—of water in fat; a certain amount of water is introduced by the mechanical agitation during the churning. It is the emulsoid character of butter that gives it its pleasant texture; melting and cooling again destroys the emulsion and with it the texture of the butter.

FOAMS.—Foams, the pleasant frothiness we look for on the surfaces of impure liquids, are of the same nature as emulsions; but the disperse phase is a gas, not a liquid.

Pure liquids do not usually foam at all readily; it is necessary to have suitable substances dissolved in them. Usually these are substances which lower the surface tension of the liquid, just as an emulsifier lowers the surface tension of the interface between the two liquids forming an emulsion. This is just as we should expect. Foaming greatly increases the liquid-air interface (that is, the interface between the liquid and the air of the foam), just as emulsification greatly increases the liquid-liquid interface. This increase in area can, as we have seen, take place more readily if the surface tension is low.

It is a thermodynamical necessity that: if a substance lowers the surface tension of a liquid in which it is dissolved, then there must be more of the substance in the surface than

in the bulk of the liquid. This is easily demonstrated for, say, a soap solution. A soap solution foams very easily, and all we have to do is to sweep off this foam and find how much soap it contains; there is a larger proportion of soap in the foam than in the bulk of the solution.

A lowering of the surface tension is, however, not a necessity for the production of foam. A striking exception is found in the case of the dye night-blue; a solution of this dye in water foams copiously. Yet the solution has a higher surface tension than pure water. This means that there must be less of the dye in the surface than in the bulk of the solution. It has been suggested that the essential condition for foaming is simply that there must be a difference in composition between the surface of the liquid and the rest of it. The fact that pure liquids hardly foam at all supports this suggestion.

Foams are of some importance industrially, and, indeed, socially. It is important that beer should have the right kind of froth, for the quality of the froth has much to do with the palatability of the beer.

Industrially, foams are of importance in the separation of minerals from one another and from impurities. Finely divided particles which are not easily wetted by water, do not sink even if they happen to be considerably heavier than water; whereas particles which are wetted by water, do sink. Thus it is easy to separate two substances from a mixture, if one of them is easily wetted by water but the other is not. It is only necessary to grind the mixture very finely and then shake it up with water. The substance which is wetted, floats, whilst the other substance does not.

The surface of water is not usually very large, so the method would not be very efficient if applied in the simple way just described. This is where foams come into the process: the water surface can be increased enormously by causing the liquid to foam; instead of the small water surface the foam gives the immense area of all the bubbles in the foam. The powdered mineral, the one which is not wetted, is taken up into the froth; the froth is swept off and the mineral is recovered from it.

Minerals which occur as sulphides are often separated from siliceous impurities by this process, the "froth-floatation process." The sulphide floats, and the siliceous matter sinks. In this process small quantities of several substances are added to the water. Substances are added : (1) To make the desired minerals float better. This is often accomplished by the addition of oil, so that the particles acquire a thin coating of oil. This makes it more difficult for the water to wet the particles. If too much oil is added it will make the particles of the mineral adhere to each other ; the particles will clump together and sink. (2) To help the sinking of the undesired siliceous matter. Mineral acids or alkalis may be used for this purpose. (3) To produce a stable froth on the water. Sometimes the oil which is used to make the minerals float better serves this purpose as well ; sometimes other substances have to be employed in addition to the oil. The mineral itself helps to stabilise the froth, in much the same way that lampblack acts as an emulsifier—because it has a tendency to accumulate at the interface. The reagents used for these three purposes must be chosen so as not to interfere with one another ; for example, the oil chosen must coat the minerals only, and not react with any of the other substances used.

Sometimes it is desirable to prevent foaming. In such cases there are several anti-foaming agents available. Anti-foaming agents are often very specific in their action ; they can be used in a few cases but are inapplicable in others. Linseed oil and alkali are, however, of quite wide application.

CHAPTER XXVII

A SURVEY OF PHYSICAL CHEMISTRY

At the beginning of the last century, chemistry and physics were two separate and distinct sciences. Perhaps the most important difference in outlook between them lay in their views on the structure of matter. The chemist had discovered the great value of the concepts of the atom and the molecule; he conceived of matter as discontinuous, consisting of a very large number of minute particles. The tendency of the physicist was to think of matter as continuous, not consisting of atoms; and he applied the same ideas to heat and to electricity, which he described as "continuous fluids."

The chemist introduced the idea of atoms and molecules because it was a convenient working hypothesis. He had no direct evidence for the existence of these minute particles; but he found that, by assuming that they do exist, it was possible to account in a simple and rational manner for all chemical compounds. The idea of valency and the discovery of the periodic table of the elements enabled him to systematise his knowledge further.

The atomic theory of matter really worked extraordinarily well; so well that it would have been surprising if, after all, it had turned out that there are no such things as atoms and molecules. It was possible, for instance, to discuss the molecule as though it had definite mechanical properties, such as resistance to deformation.

But there was always an essential limitation to purely chemical methods of attacking these problems of structure. For one thing, chemical methods cannot take us beyond the atom in our analysis; definitely physical methods must be used to work out how the atoms themselves are built up. For another, the chemist has to treat atoms and molecules

en masse ; physical ideas must be introduced before it is possible to deal with the behaviour of single atoms and molecules.

A revolutionary change in physical and chemical ideas began toward the end of the last century with the discovery of the electron and of radioactivity, followed shortly afterwards by the idea, due to Planck, that energy exists in small "packets" or quanta. As a result of these discoveries it was found possible to work out the structure of the atom. The first idea was of electrons revolving round a small positive nucleus, on the analogy of the solar system. Then it was found that the positive charge on the nucleus increases one by one from element to element ; the properties of an element depend on the charge on the nuclei of its atoms. This discovery provided a complete justification for the periodic table ; it cleared away doubts and anomalies, and showed the few gaps as yet unfilled by known elements. It showed, too, how the existence of isotopes may come about ; and it pointed the way towards the transmutation of the elements, a process which has since been accomplished on a small scale.

It was Bohr who first investigated the orbits of the electrons revolving round the nucleus. The first great success of his theory was in predicting the exact positions of the lines in the hydrogen spectrum. Subsequent workers introduced modifications and refinements into the Bohr theory, until eventually there arose the idea that every electron in an atom has four quantum numbers associated with it. The electronic orbits could be sorted out into their various shells and subgroups by means of the Pauli exclusion principle.

Such was the picture of the atom produced by the physicist. The chemist was soon able to apply this picture to his own problems, particularly to the problem of how atoms are linked together to form molecules. Kossel explained the electrovalent link by supposing that atoms tend to gain or lose electrons until they have acquired an inert gas configuration ; and Lewis conceived of the covalent link as consisting of a pair of electrons shared by two atoms.

These ideas cleared up many difficulties about valency. Before the electronic theory of valency, no very clear distinction was drawn between ionised and covalent links. It was not clearly realised, for instance, that a covalent link has a definite direction in space, whereas an ionised link has no such definite direction. The co-ordinate link was another concept introduced by the electronic theory; previously many co-ordinate links had been written as double links.

Once the nature of chemical linkage was established in this way, it was possible to put stereochemistry on a more satisfactory basis. Moreover, many new methods have recently become available for investigating the space arrangements of atoms in molecules, and the forces between the atoms. The variety of modern methods is indeed extraordinary. In the first place there are the so-called "classical" methods, which depend on the investigation of certain kinds of isomerism—optical isomerism and geometrical isomerism. Then there is the method of burning a compound to find out how much energy is given out during the process; if the molecule is in a state of strain it will contain an abnormally large amount of energy, which is readily detected during the combustion. More modern methods of investigating problems of stereochemistry include the determination of dipole moments, the study of molecular spectra in general and of Raman spectra in particular, and all the various X-ray and electron-ray methods of studying crystals and vapours. Perhaps the most surprising of all is the method depending on the study of surface films on liquids.

There is an astonishing variety of methods available. Yet they all converge on the same results; they are consistent with one another, so we are justified in placing the greatest confidence both in the measurements themselves and in the underlying theory. The molecule is now firmly established as a reality; it is so real that we can talk confidently of the "squashing together" of molecules in surface films, for example. It is so real, indeed, that models of molecules have actually been constructed from balls held together by springs; these models showed just the charac-

teristic vibrations we should expect from the Raman spectra of the compounds in question.

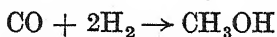
Having obtained much useful and precise information on the subject of the structure of molecules, we can apply that knowledge to the study of chemical reactions. It should be realised, however, that until very recently the tendency has been all the other way : to argue back from the reactions of a compound to the structure of its molecules. This is what often happens in science : we do not proceed from the proton, the neutron, and the electron to the atom, and then to the molecule, and from there to the subject of chemical reactions. Instead we fill in the whole picture bit by bit, until at last the different parts of the picture join up and we can view the subject as a whole.

In the early days of chemistry it was considered sufficient to know the initial and final products of a reaction and briefly the conditions under which it takes place. Physical chemistry seeks for much fuller information. We want to know the speed of the reaction and how the speed depends on the concentration, how it depends on the pressure, and how it depends on the temperature. We want to know whether the reaction is homogeneous, taking place throughout the whole mass of the reacting substances, or whether it is heterogeneous and confined to surfaces. We want to know whether the apparent reaction is the real reaction or only the net result of a series of reactions. And finally we want to know why the reaction occurs at all—what are the essential energy conditions, and how the reaction results from the movements of the electrons in the molecules.

This fuller knowledge of chemical reactions can be used to suggest improvements in technique, both in the laboratory and in chemical industry. It does so by indicating the conditions in which reactions can take place most favourably. In the production of ammonia, for example, the older method was to test each set of conditions empirically ; each set that was unfavourable was rejected and the best was chosen out of those that remained. This method eventually gave the desired result ; but it was cumbrous and wasteful. When a similar problem is being investigated to-day, the

methods of thermodynamics are used to calculate the right conditions for a good yield, and the actual experimental work is reduced to a minimum.

It is a great advantage to start like this with some knowledge of the most favourable conditions, particularly in a case like the production of methyl alcohol from water-gas (a mixture of carbon monoxide and hydrogen). The reaction is :



Experimental investigation of this reaction is both difficult and expensive because it is necessary to use high pressures and high temperatures. Thermodynamics enables us to calculate beforehand the favourable conditions of temperature and pressure, so that the amount of experimental work is greatly reduced.

One of the most interesting branches of the science of chemical reactions is the subject of catalysts. The term was introduced at a time when little was known of how catalysts can accelerate reactions. Now that the mechanism of catalysis has been elucidated, we find that a number of diverse phenomena are included under the same head.

Of particular importance are those catalysts that act by adsorbing the reactants, so that the actual reaction takes place on the surface of the catalyst. The majority of industrial processes introduce a catalyst of this sort at some stage or other. As a result of the study of adsorption and surface reactions, we no longer have to rely on a happy accident to find a catalyst for any particular reaction. The subject is still in a semi-empirical stage, but we can generally predict at least what kind of catalyst will be suitable for any particular purpose. We know, too, how to deal with such problems as catalyst poisoning and we know how to obtain our catalyst in as active a form as possible.

Closely connected with surface chemistry is the chemistry of colloids. Colloids are substances which are composed of minute particles, yet not so excessively minute as to be of molecular size. A colloidal solution, for example, consists of small particles of solid dispersed throughout a liquid. Relatively to their volume, small particles have an enormous

surface area; an ounce of ramie fibre contains particles (micelles) of colloidal size, whose total surface area is about 160,000 square feet. So the problem of what happens at surfaces arises in an acute form when we come to study colloids.

Physical chemistry is rapidly building up a more exact framework for the whole subject of chemistry. We have had examples of this in the study of the structure of molecules, the speed of reactions, and the chemistry of surfaces. To this list we can add the subject of solutions of electrolytes, where the Debye-Hückel theory has placed all our ideas on a new footing; and thermodynamics and the phase rule, which enable us to investigate chemical equilibria and the stability of chemical compounds. Physical chemistry is carrying the analysis of chemical problems to much greater lengths than was formerly possible; it is placing the whole subject on a quantitative instead of merely a qualitative basis. In brief, it is creating a chemistry which for exactness and certainty is as much in advance of the older chemistry as the chemistry of the last century was in advance of that of the alchemists.

A SHORT BIBLIOGRAPHY

So far as the authors are aware, the present book treats the subject of physical chemistry from a new point of view. Most of the books in the following list are written primarily for chemists, so it will be realised that they are of a more advanced standard than this book. But this should not discourage the reader; there is much excellent reading matter in the books listed here.

ADAM, N. K. : *The Physics and Chemistry of Surfaces* (O.U.P., 17/6).

This book can be strongly recommended. It is very readable, and the writer has treated the subject as non-mathematically as possible.

ASTBURY, W. T. : *Fundamentals of Fibre Structure* (O.U.P., 8/6).

This book starts with a simple explanation of the production of X-ray photographs of crystals and other solids, and then proceeds to consider the structure of wool and other fibrous materials. It was written originally for textile workers, so it presupposes very little knowledge of chemistry.

ASTON, F. W. : *Mass-Spectra and Isotopes* (Edward Arnold, 15/-).

This is the standard account of the subject. The ordinary reader will probably find Parts I. and IV. the most interesting.

DAVIES, C. W. : *The Conductivity of Solutions* (Chapman and Hall, 15/-).

This is an advanced text-book, but the reader with a knowledge of, say, elementary calculus should find it interesting. Be sure of getting the latest (the second) edition.

GLASSTONE, S. : *Recent Advances in Physical Chemistry* (Churchill, 15/-).

This book covers much the same ground as the

present book, but from a considerably more advanced point of view.

HEDGES, E. S.: *Colloids* (Edward Arnold, 12/6); and *Protective Films on Metals* (Chapman and Hall, 15/-).

These two books are both excellently written and well worth reading.

HINSHELWOOD, C. N.: *The Kinetics of Chemical Change in Gaseous Systems* (O.U.P., 15/-).

The first chapter is very mathematical; having skipped this, the reader will find the rest of the book of great interest; it is excellently written. Make sure of getting the latest (the third) edition.

JAMES, R. W.: *X-ray Crystallography* (Methuen, 2/6).

A good introduction to a difficult and mathematical subject.

JOHNSON, R. C.: *Spectra* (Methuen, 2/6).

The subject is again somewhat mathematical; but for those who can manage it, this book is to be recommended.

PANETH, F.: *The Radio-Elements as Indicators* (McGraw-Hill, 12/6).

An excellent account of a very interesting subject.

RAWLING, S. O.: *Infra-red Photography* (Blackie, 3/6).

This book deals almost entirely with the practical side of the subject; it is very interesting.

SIDGWICK, N. V.: *The Electronic Theory of Valency* (O.U.P., 15/-), and *The Covalent Link in Chemistry* (O.U.P., 9/-).

Both these books are eminently readable; the author has a genius for clarifying complex and difficult ideas.

STYLE, D. W. G.: *Photochemistry* (Methuen, 2/6).

This book presents in a lucid and concise form the salient points of photochemistry.

THOMSON, G. P.: *The Atom* (Home University Library, Thornton Butterworth, 2/6).

A very good popular account of such subjects as the Bohr theory, radioactivity, X-ray crystallography, written from the point of view of the physicist.

WORSNOP, B. L.: *X-rays* (Methuen, 2/6).

A good short account of the subject.

A VOCABULARY OF CHEMICAL TERMS

ATOM. **MATTER** consists of minute particles called **atoms**. There are about ninety chemically distinct kinds of atoms ; it is only with very great difficulty that one kind of atom can be changed into another. A **molecule** consists of two or more atoms linked together ; these atoms may be of the same kind or of different kinds. In a chemical **element** the atoms are all of the same kind, so that there are as many different elements as there are kinds of atoms. A chemical **compound** consists of molecules containing two or more different kinds of atoms ; in any pure compound all the molecules are alike. The **formula** of a compound tells us which atoms compose a molecule of the compound. The formula of water is H_2O ; this formula shows that each molecule of water contains two atoms of hydrogen and one of oxygen. Slaked lime has the formula $\text{Ca}(\text{OH})_2$; the formula is written in this way, and not CaO_2H_2 , to draw attention to the fact that OH is regarded as a group ; this group occurs intact in many compounds, and there are numerous such groups.

The weight of a hydrogen atom is 1.5×10^{-24} grams. This weight used to be taken as the unit for measuring the weights of the atoms of other elements. The weights of atoms, expressed in this scale, were called **atomic weights** ; the weights of compounds were called **molecular weights**. Thus the weight of the oxygen atom is about 16 times the weight of the hydrogen atom ; hence the atomic weight of oxygen is (about) 16. Water, H_2O , has a molecular weight of $18 (2 \times 1 + 16)$. For several reasons the weight of the hydrogen atom was found to be inconvenient as a unit ; the weight of an oxygen atom is now taken as 16 exactly ; the atomic weight of hydrogen on this scale is 1.008.

It is convenient to have a larger unit than the atom or molecule. The units chosen are the **gram-atom** and **gram-molecule**. Thus the atomic weight

- GRAM-MOLECULE. of oxygen is 16, so a gram-atom of oxygen is 16 grams of oxygen. The molecular weight of water is 18, so a gram-molecule of water is 18 grams of water.
- VALENCY. **Valency** is a rather vague term. Roughly we may say that it is the number of chemical links an atom can form with other atoms. Hydrogen has a valency of one. Since hydrogen chloride is $\text{H}-\text{Cl}$, chlorine also has a valency of one. In water, H_2O , the oxygen atom forms a link with each of the hydrogen atoms; it is divalent. In ammonia, NH_3 , the nitrogen atom is trivalent. In nitrogen trioxide, N_2O_3 , we have six links from the two trivalent nitrogen atoms to the three divalent oxygen atoms. The valency of an element may be different in different compounds. Thus in phosphorus trichloride, PCl_3 , the phosphorus is trivalent; whereas in phosphorus pentachloride, PCl_5 , it is pentavalent.
- INERT GASES. The **inert gases** (helium, neon, argon, krypton, xenon, emanation) occur in the atmosphere; helium and emanation are also obtained from radioactive sources. Their most distinctive property is their lack of chemical activity; they form practically no compounds at all. The **alkali metals** (lithium, sodium, potassium, rubidium, caesium) are light, soft metals which react readily with oxygen and water. The compound formed by reaction with water is a caustic alkali. Each of the alkali metals has one electron in the outermost shell of orbits.
- ALKALI METALS. The **alkaline earth metals** (calcium, strontium, barium, radium), when burnt in air, give oxides which are alkaline in character but not caustic. They are less reactive than the alkali metals; each has two electrons in the outermost shell. The **rare earth metals** (lanthanum, cerium, praseodymium, neodymium, illinium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutecium) are very similar to each other in their chemical properties. They are so similar that they are all put in the same place in the periodic table. So far as compound formation is concerned they behave as if they had each three electrons in the outermost shell of orbits and eight in the shell below. The **halogens** are fluorine, chlorine, bromine, iodine. The name means salt-forming; the salts come from the sea. Each has seven electrons in the outermost shell. The **transition elements** (iron, cobalt, nickel; ruthenium,

rhodium, palladium; osmium, iridium, platinum) are arranged in three series of three. They are similar in properties, especially within each series. The whole group is sometimes called the iron group, the term "transition elements" being applied to a much larger group of elements.

- ACID.** An acid is any neutral molecule which gives hydrogen ions in a suitable solvent. (This term has been extended to include charged molecules (ions) which yield hydrogen ions.) Acids often have a sour taste and usually turn blue litmus red. An
- ALKALI.** alkali is any substance which can give hydroxyl (OH) ions when dissolved in a suitable solvent. Alkalis usually turn red litmus blue. Alkalis react with acids, they "neutralise" them, giving com-
- SALT. BASE.** pounds known as salts. The term base includes all substances which react with acids to give salts, whether they are soluble (alkalis) or insoluble. The following table gives the names of some of the commoner salts, along with the acids from which they are derived:

<i>Acid.</i>	<i>Salts.</i>	
hydrofluoric	fluorides	These salts are collec- tively called halides.
hydrochloric	chlorides	
hydrobromic	bromides	
hydriodic	iodides	
sulphuric	sulphates	
nitric	nitrates	
phosphoric	phosphates	
carbonic	carbonates	

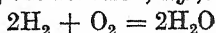
- ALLOY.** Alloys are mixtures or compounds of two or more metals; they are composed exclusively of metals. Brass, for example, is an alloy of copper and zinc.
- AMALGAM.** An amalgam is an alloy in which one of the metals is mercury.
- PHASE.** A phase is any portion of a system which has the same composition throughout (it is homogeneous). Thus with water and steam there is a liquid phase and a gas phase. With a solution of common salt there may be a solid phase (undissolved salt), a liquid phase (the solution), and a vapour phase. If ether and water are shaken up the mixture separates out into two layers; each layer is a phase—one phase is nearly all ether and the other phase nearly all water. The interface is the boundary between
- INTERFACE.**

SURFACE TENSION. two phases. At every interface there is a force, called the **surface tension**, which tends to make the interface contract.

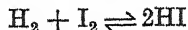
CRYSTAL. Solids can be either crystalline or amorphous. The characteristic feature of **crystals** is that they have a regular geometric structure. **Amorphous** substances have no such regular structure. Some substances which are apparently amorphous turn out to consist of minute crystals; they are said to be **microcrystalline**.

MICRO-CRYSTAL. The commonest kinds of solution are those in which a solid is dissolved in a liquid. In this case the liquid is called the **solvent** and the solid the **solute**. When a gas is dissolved in a liquid the gas is the solute. When a liquid is dissolved in a liquid the terms solvent and solute are meaningless. The **concentration** of a solution is the proportion of solute to solvent; for instance, the number of grams of solute present in 1000 grams of solvent. A **dilute**, or weak, solution contains only a small proportion of the solute. A **concentrated**, or strong, solution contains a large proportion of the solute.

REACTION. When a chemical **reaction** takes place the molecules concerned are different after the reaction from what they were before it. For instance, molecules of hydrogen and oxygen undergo a reaction, or simply "react together," to give molecules of water. The substances which react are called **reactants**. A chemical equation is a convenient way of summarising the reaction, *e.g.*,



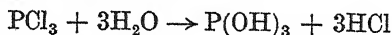
REACTANT. This equation explains that two molecules of hydrogen (H_2) react with one molecule of oxygen (O_2) to give two molecules of water (H_2O). (An arrow is sometimes used instead of the = sign.) A **reversible reaction** is a reaction which can take place in either direction. For example, the reaction between hydrogen and iodine, to give hydrogen iodide, is reversible.



EQUILIBRIUM. The sign \rightleftharpoons indicates that the reaction can take place in either direction. When hydrogen iodide is being formed (by the combination of hydrogen and iodine) as quickly as it is being decomposed into hydrogen and iodine, we say that **equilibrium** has been reached.

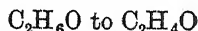
DISSOCIA-
TION.

Certain types of reaction have special names. **Dissociation** is the breaking up of a molecule into smaller molecules. Ammonium chloride, NH_4Cl , dissociates into ammonia, NH_3 , and hydrogen chloride, HCl . The name dissociation is restricted to cases where the products recombine in suitable conditions. The term **decomposition** is used for reactions of this sort, whether the products recombine or not. A compound is said to be **hydrolysed** when it reacts with water in such a way that it breaks up and forms two compounds, one with the hydrogen of the water and the other with the hydroxyl. Thus :



OXIDATION.

Oxidation originally meant increasing the proportion of oxygen in a compound (the oxygen content); for example, sulphur dioxide, SO_2 , was changed to sulphur trioxide, SO_3 , by oxidation. The term was extended to mean also decreasing the hydrogen content; for example, in the oxidation of alcohol to aldehyde :



REDUCTION.

It has also been extended to cover any reaction that involves the removal of an electron; for example, the oxidation of the ferrous ion to the ferric ion—

HYDRO-
GENATION.

Fe⁺⁺ to Fe⁺⁺⁺. **Reduction** is the reverse process to oxidation: the addition of hydrogen, the removal of oxygen, or the addition of an electron. **Hydrogenation** is the introduction of hydrogen into a compound, and **chlorination** is the introduction of chlorine.

CHLORINA-
TION.

CATALYST.

Chemical reactions are often accelerated, or less often retarded, by the addition of foreign substances. Substances which accelerate a reaction are called **catalysts**; those which retard a reaction are called **negative catalysts** or **inhibitors**.

NEGATIVE
CATALYST.

INHIBITOR.

ELECTRIC

CURRENT.

An **electric current** in a metal is a flow of minute charged particles (electrons) through the metal. For a current to flow from one point to another there must be a difference in **potential** between the two points. The current flows from the higher potential to the lower, just as water flows from a place of higher pressure to a place of lower pressure. Differences in potential are very often measured in volts.

POTENTIAL.

RESISTANCE. In every material there is some **resistance** to the

CONDUCTIVITY. flow of an electric current. (Resistance is usually measured in ohms.) The **conductivity** is the reciprocal of the resistance ($\frac{1}{\text{resistance}}$); it is a measure of the ease with which a substance carries electricity.

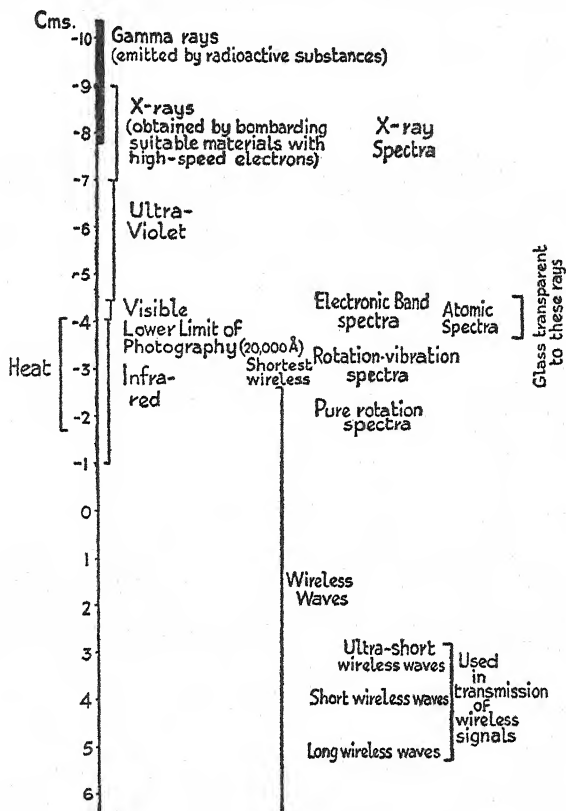


FIG. 87.—The complete range of light-waves. The scale is logarithmic.

**ELEC-
TROLYTE.**

Some solutions conduct electricity; such solutions are called **electrolytes**. (The name "electrolyte" is also used for the solid which is dissolved.) The electrolyte is ionised; it is split up into positively charged ions called **cations**, and negatively charged ions called **anions**. To pass a current through a solution of an electrolyte two **electrodes** must be introduced into the solution. The negative

CATION.
ANION.
**ELEC-
TRODE.**

CATHODE. electrode (the **cathode**) attracts the cations; the
ANODE. positive electrode (the **anode**) attracts the anions.
And so a current consisting of cations moving in one
direction and anions moving in the other passes
through the solution.

WAVE-LENGTH. In a wave motion the distance from crest to crest
of the waves is known as the **wavelength**. In the
ÅNGSTRÖM case of light-waves the wavelength is measured in
UNIT. **Ångström units**. This unit is 10^{-10} of a metre. The
FRE-**frequency** is the number of crests which pass a given
QUENCY. point per second. The frequency and the wave-
length are so related that their product is equal to
the velocity of the waves. Ordinary white light
consists of all wavelengths within a certain range.
The different wavelengths can be sorted out into a
SPECTRUM. **spectrum**, where each wavelength is represented by
a vertical line. The diagram on p. 287 shows the
complete range of light-waves.

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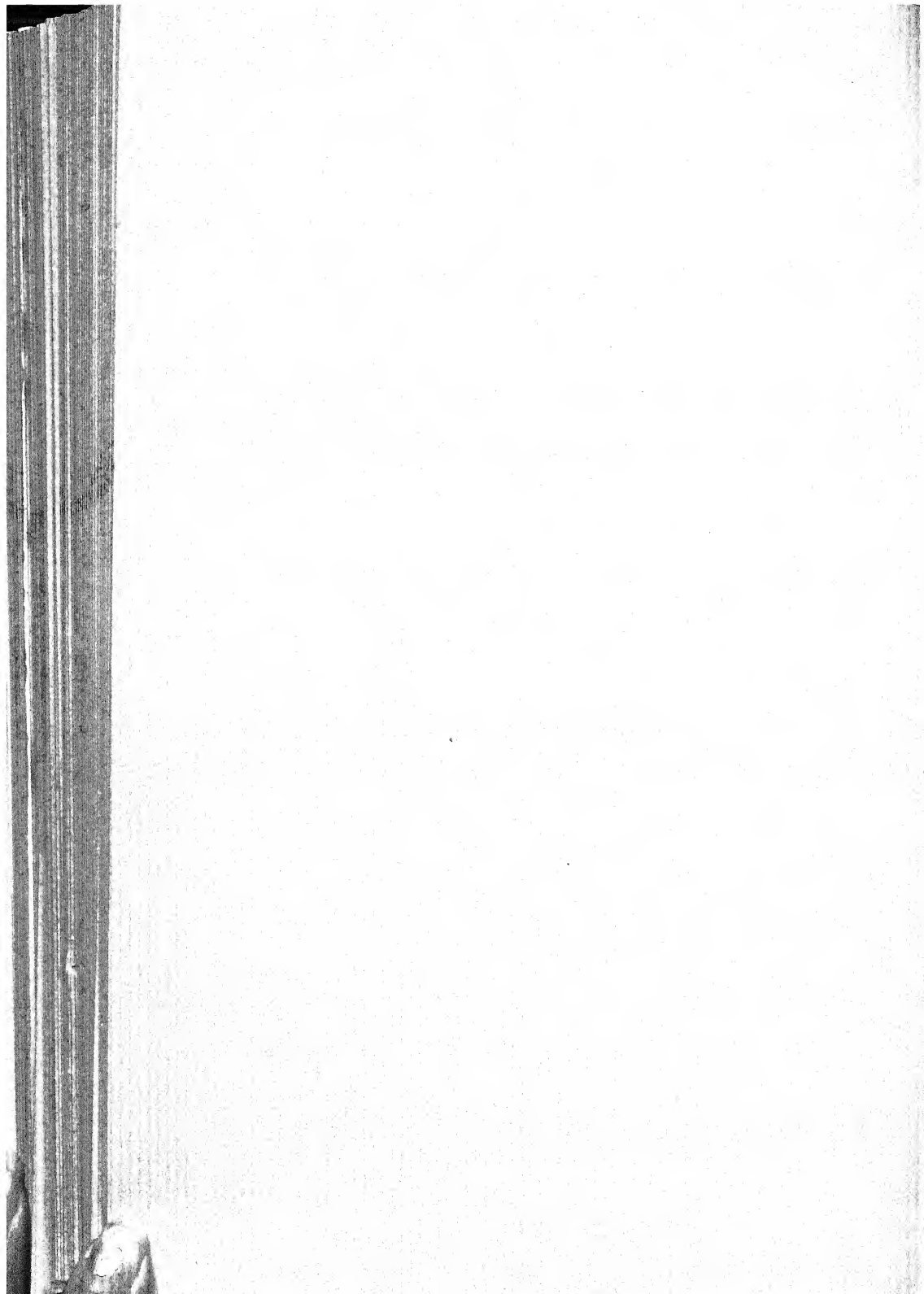
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